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September 1984

DESCRIPTION AND OPERATION OF A THERMAL DECOMPOSITION UNIT-GAS CHROMATOGRAPHIC SYSTEM

by

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Cooperative Agreement CR-807815

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Before acceptable incineration procedures can be fully developed for hazardous organic materials, precise information is often needed concerning their thermal decomposition properties. In response to this need, a laboratory-scale thermal decomposition unit-gas chromatographic system (TDU-GC) has been designed and assembled to provide data rapidly and safely on the gas-phase thermal decomposition behavior of organic substances. This system has been designed to accommodate a wide variety of organic materials which range from pure substances to very complex industrial organic waste mixtures. This report describes the design and operation of the TDAS (Thermal decomposition analytic systems).

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes the design, operation, and use of the Thermal Decomposition Unit-Gas Chromatographic (TDU-GC) System. This system has been extensively employed by EPA in the development of thermal decomposition data for hazardous compounds regulated under the Resource Conservation and Recovery Act of 1976 (RCRA).

This report will be instructive to others who wish to assemble and operate such systems for the purpose of assessing thermal decomposition properties, destruction kinetics, and incomplete combustion products for hazardous compounds.

David G. Stephen
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

The disposal of toxic substances has been recognized for many years as a serious problem. Accordingly, many procedures had been proposed for the safe disposal of toxic organic wastes. Controlled high-temperature incineration is recognized as one of the most promising methods for the permanent disposal of industrial organic wastes.

Before acceptable incineration procedures can be fully developed for the immense variety of organic materials, precise information is needed concerning their thermal decomposition properties. In response to this need, laboratory-scale thermal instrumentation has been designed and developed for experimentally determining the high-temperature gas-phase decomposition properties of toxic organic substances.

A thermal decomposition unit-gas chromatographic system (TDU-GC) has been designed and assembled to provide data rapidly and safely on the gas-phase thermal decomposition behavior of organic substances. This system has been designed to accommodate a wide variety of organic materials which range from pure substances to very complex industrial organic waste mixtures. Data obtained with the TDU-GC should provide guidance with respect to the eventual incineration of numerous industrial organic wastes.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AFS -- amperes full scale
AMP -- operational amplifier
CO_2 -- carbon dioxide
CRF -- Combustion Research Facility
DDT -- dichloro-diphenyl-trichloroethane
EPA -- U.S. Environmental Protection Agency
GC -- gas chromatography
Ga -- gauge
HCl -- hydrochloric acid
H_2O -- water
ID -- inside diameter
OD -- outside diameter
OTC -- open tubular column
PAH -- polynuclear aromatic hydrocarbon
PIC -- product of incomplete combustion
POHC -- principal organic hazardous constituent
RE-CTE -- random entry - controlled thermal exposure
RTD -- resistance thermometer
TDAS -- thermal decomposition analytical system
TDU -- thermal decomposition unit
TDU-GC -- thermal decomposition unit-gas chromatographic system
TECO -- Theall Engineering Company
VDC -- volts direct current
VOM -- volt ohm meter
cm -- centimeters
min -- minutes
mm -- millimeters
ms -- milliseconds
mv -- millivolts
psig -- pounds per square inch gauge
sec -- seconds
tc -- thermocouple

SYMBOLS

°C -- degrees Celsius

F -- gas volumetric flow rate

F_o -- outlet flow

°K -- degrees Kelvin

KΩ -- kilohms

L -- length

M -- meter

Rl -- transfer line flow resistance

R_q -- reactor assembly resistance to gas flow

R_r -- restrictor flow resistance

R_t -- trap flow resistance

R_3 -- electrical resistor

R_4 -- electrical resistor

T_o -- temperature at ambient outlet

T_1 -- transport temperature

T_2 -- exposure temperature

$\bar{T}$ -- average temperature

$\bar{T}_2$ -- average reactor temperature

V -- volume, and voltage

V_o -- gas volume at ambient conditions

V_1 -- operational amplifier voltage

V_2 -- operational amplifier voltage, volume of quartz tube interior

p_o -- ambient pressure

p_d -- differential pressure

p_1 -- pressure at reactor exit

p_2 -- internal reactor pressure

r -- reactor tube radius

t -- time

t_r -- residence time

$\bar{t}_r$ -- mean residence time

σ_t -- standard deviation of Gaussian function

ψ_t -- residence time probability

Ω -- ohms resistance

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SECTION 1

INTRODUCTION

Numerous procedures have been proposed for the disposal of the vast quantities of industrial organic wastes that are produced annually. Some procedures are temporary. Many of these consist essentially of containment methods. Other disposal methods are more permanent in nature, as they produce chemical changes in the organic substance with the intention of rendering the material safe. Of the various methods involved with changing the structure of the toxic organic molecules, chemical and thermal techniques are the most applicable.

One of the most promising methods for the permanent disposal of hazardous organic wastes is controlled high-temperature incineration. Both land-based incineration and incineration on ocean-going vessels have been utilized for the disposal of organic industrial wastes.

Before methods can be developed for the disposal of the immense variety of organic materials, precise information is needed concerning their thermal decomposition properties. Much information is yet to be obtained about the thermal decomposition of these organic materials and the nature of the decomposition products formed. It has been demonstrated (1-4) that this basic information can be obtained in the laboratory using very small quantities of sample,micrograms or even less.

There are many advantages to generating fundamental gas phase thermal decomposition data in the laboratory. First, data generated in the laboratory can be much more precise and comprehensive than thermal decomposition data generated in field-scale studies. In addition, it is anticipated that these thermal decomposition experiments can be conducted safely in a properly equipped laboratory. There would be a much higher element of risk if the initial studies were conducted in larger throughput units. Finally, laboratory thermal decomposition data can be obtained economically and in a short period of time.

Once the thermal decomposition properties of a particular material have been characterized in the laboratory, the preliminary decision can be made as to whether high-temperature incineration is a viable disposal route for that particular material. If no adverse characteristics are detected during the laboratory experiments then, with due caution, the material can be subjected to larger-scale thermal decomposition studies. However, if the laboratory data indicated difficulties or problem areas, then incineration is probably not a viable disposal method for that particular substance.

At the University of Dayton Research Institute, numerous laboratory-scale thermal decomposition studies of various organic materials have been conducted. These experiments have been performed using recently developed thermal decomposition instrumentation. Most of this work has been accomplished using a previously described (5-7) thermal decomposition analytical system (TDAS).

This report describes a versatile thermal instrumentation system that is very similar to the TDAS. Specifically, this latest instrumentation assembly is a thermal decomposition unit-gas chromatographic (TDU-GC) system, and its operation is described relative to conducting laboratory experiments with industrial organic waste samples and other organic compounds. The TDU-GC has been designed specifically to provide laboratory-scale gas-phase thermal decomposition data quickly and in a safe manner.

SECTION 2

CONCLUSIONS

Two thermal decomposition unit-gas chromatographic (TDU-GC) systems have been designed and assembled. One of these systems is intended for continuing basic studies of gas phase thermal decomposition of organic compounds. The other TDU-GC system is for use at the U.S. Environmental Protection Agency's Center-Hill Research Facility in Cincinnati, Ohio where it will be supporting in-house thermal decomposition studies.

With these laboratory systems, the thermal decomposition behavior of industrial organic wastes, individual organic compounds and a wide assortment of other organic substances can be experimentally evaluated. The effects of the major gas phase thermal decomposition variables can be investigated with the TDU-GC.

These laboratory systems have a number of specific features incorporated into their design, as follows:

- With the closed continuous design concept and the glove-boxed sample entry of this system, toxic samples can be safely tested.
- Samples can be subjected to a very precise thermal exposure in the TDU-GC. At selected reactor temperatures ranging from 200° to 1150°C, the maximum temperature variation is less than ±2°C.
- The TDU-GC is capable of subjecting a sample to a precise mean residence time ranging from 0.25 to 5.0 seconds. In addition, this system provides a narrow Gaussian residence time distribution.

- With the flexibility designed into the TDU-GC, thermal decomposition studies can be conducted using pure organic substances or complex organic mixtures, and only small quantities of sample are needed (micrograms). Samples can be either gases, liquids, or solids. In addition, these samples can be subjected to thermal decomposition studies in any of a wide variety of atmospheres.
- Analyses of the thermal decomposition products are performed through the use of a versatile high-resolution gas chromatograph and a variety of sensitive detectors.
- The TDU-GC can provide basic thermal decomposition data rapidly and economically.

SECTION 3

RECOMMENDATIONS

In view of the numerous industrial organic compounds and mixtures that need to be subjected to permanent disposal, it is recommended that the high-temperature gas-phase thermal decomposition behavior of these organic materials be evaluated using the laboratory-scale thermal decomposition unit-gas chromatographic (TDU-GC) system. This thermal instrumentation system has been designed for the efficient examination and safe handling of a wide variety of organic substances. It is recommended that for these various complex organic mixtures that laboratory-scale data be obtained prior to subjecting large quantities of these materials to control high-temperature incineration.

It is further recommended that the TDU-GC be utilized for data base generation, such as, studying the thermal decomposition behavior of hazardous organic compounds and determining the formation of products of incomplete combustion (PICs). As many variations in conditions can occur throughout the various regions of a large incineration system, it is recommended that the effects of different incineration variables be studied using the TDU-GC system.

SECTION 4

BACKGROUND

Appropriate incineration of toxic organic wastes requires very high temperatures, sufficient gas-phase residence time, ample quantities of oxygen, and extensive gas-phase mixing. In addition, there must be sufficient control over the various incineration variables. To insure that parent organic substances and the various products of incomplete combustion (PICs) are subjected to sufficient thermal exposures, it is common practice in incineration technology to utilize large-volume afterburners for accomplishing complete destruction.

Today one of the most popular controlled high-temperature incinerator designs for the disposal of organic wastes is the rotary kiln/afterburner assembly. This type of incineration facility can deal with practically any type of organic waste material. Large rotary kiln/afterburner facilities are relatively common in Europe, and they are being introduced at various sites in the United States.

Recommended guidelines for operating high-temperature incinerators have been prepared (9) and in the past these guidelines recommended the controlling of exposure temperature, residence time, and excess oxygen levels for obtaining appropriate operation of the incinerator. At the present time, it is fair to say that considerably more information is needed concerning the effects of various incineration variables relative to the extent of thermal destruction and also with respect to the levels of emissions that escape the incinerator afterburner. The U.S. Environmental Protection Agency has recognized this need for additional information, and that is one of the major reasons for establishing the Combustion Research Facility (8) in Jefferson, Arkansas. This particular facility will be studying, on the pilot-scale level, the various incineration parameters that affect combustion efficiency and effluents.

At the University of Dayton, laboratory-scale thermal decomposition studies have been in progress since 1974. These laboratory studies have used specially designed laboratory-scale instrumentation for studying the thermal decomposition behavior of numerous organic substances. These studies have been conducted using high-temperature quartz tubular reactors for the gas-phase decomposition of organic species. Descriptions of these laboratory instrumentations have been documented in various EPA reports (1,4,5,11), and this design information has also been presented before numerous environmental conferences (6,7,11-18).

As examples of earlier thermal instrumentation systems, Figure 1 shows schematics of a discontinuous thermal system which was initially used for studying the thermal decomposition behavior of chlorinated pesticides. Figure 2 is an artist's rendering of the thermal decomposition analytical system (TDAS) and Figure 3 is a block diagram of the same system.*

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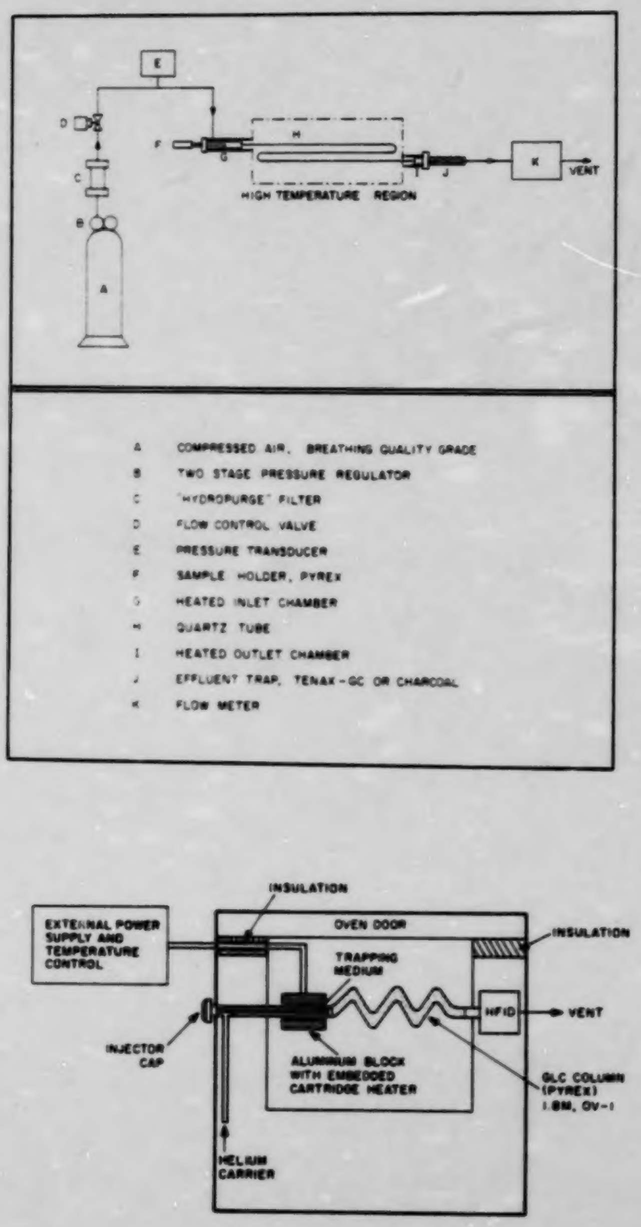
*In 1983, the TDAS was modified and reconfigured. It now includes a glove-boxed sample insertion region, a subambient programmed temperature GC, and a glass jet interface between the GC and the mass spectrometer.


E
D
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VENT
C
B
A
HIGH TEMPERATURE REGION
A COMPRESSED AIR, BREATHING QUALITY GRADE
B TWO STAGE PRESSURE REGULATOR
C "HYDROPURGE" FILTER
D FLOW CONTROL VALVE
E PRESSURE TRANSDUCER
F SAMPLE HOLDER, PYREX
G HEATED INLET CHAMBER
H QUARTZ TUBE
I HEATED OUTLET CHAMBER
J EFFLUENT TRAP, TENAX-GC OR CHARCOAL
K FLOW METER
INSULATION
EXTERNAL POWER SUPPLY AND TEMPERATURE CONTROL
OVEN DOOR
INSULATION
TRAPPING MEDIUM
HFID
VENT
INJECTOR CAP
ALUMINUM BLOCK WITH EMBEDDED CARTRIDGE HEATER
GLC COLUMN (PYREX) 1.8M, OV-1
HELIUM CARRIER

Figure 1. Schematic of a Discontinuous Thermal System.

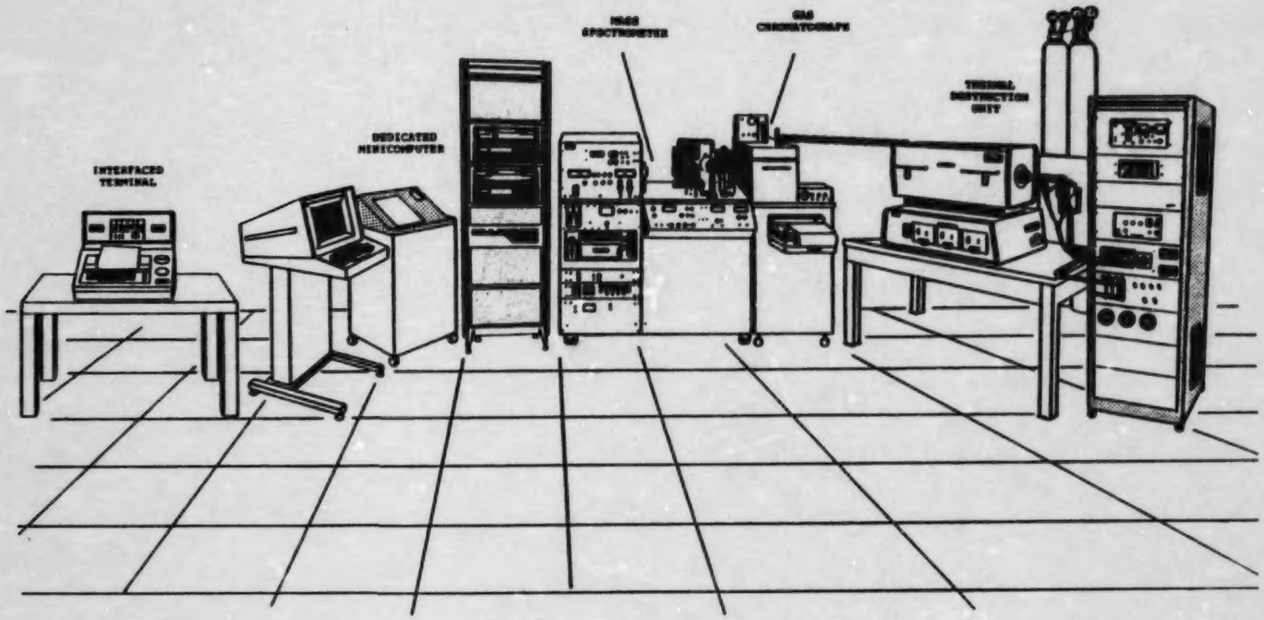
INTERFACED TERMINAL
DEDICATED MINICOMPUTER
MASS SPECTROMETER
GAS CHROMATOGRAPH
THERMAL DESTRUCTION UNIT

Figure 2. Artist's Rendering of Assembled TDAS.

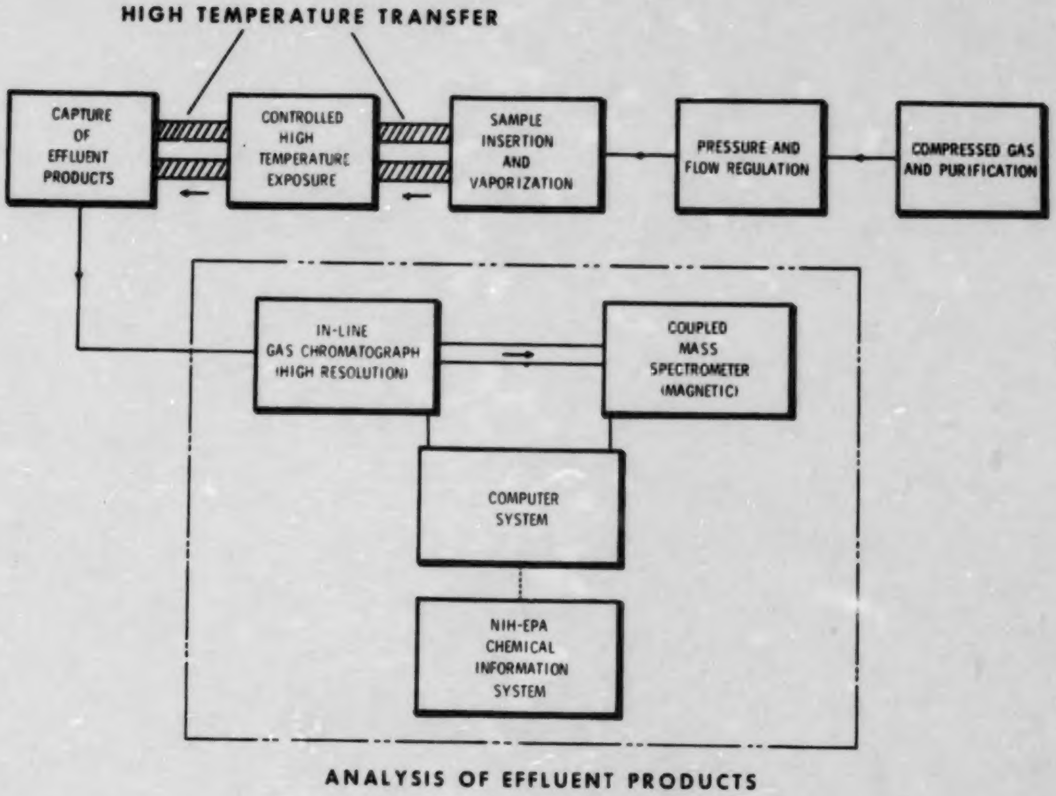
HIGH TEMPERATURE TRANSFER
CAPTURE OF EFFLUENT PRODUCTS
CONTROLLED HIGH TEMPERATURE EXPOSURE
SAMPLE INSERTION AND VAPORIZATION
PRESSURE AND FLOW REGULATION
COMPRESSED GAS AND PURIFICATION
IN-LINE GAS CHROMATOGRAPH (HIGH RESOLUTION)
COUPLED MASS SPECTROMETER (MAGNETIC)
COMPUTER SYSTEM
NIH-EPA CHEMICAL INFORMATION SYSTEM
ANALYSIS OF EFFLUENT PRODUCTS

Figure 3. Block Diagram of TDAS.

With the use of this laboratory instrumentation, a wide variety of environmentally important organic compounds have been studied with respect to their thermal decomposition behavior. Table 1 lists most of the compounds that have been studied thus far at the University of Dayton with respect to their gas-phase thermal decomposition behavior.

Laboratory-scale studies are also ideally suited for identifying and studying the various parameters and variables that affect gas-phase high-temperature thermal decomposition behavior. Table 2 lists those major gas-phase variables which have been identified thus far as having profound effects upon the extent of thermal decomposition. Certainly, exposure temperature is a very important variable, and the time that a gas-phase species is subjected to this high-temperature is also important. We have also theorized and determined the importance of residence time distribution. The pressure of the gas phase has also been found to be a variable with respect to extent of thermal decomposition. Temperature gradients have long been recognized as an important variable with respect to incineration efficiency. The composition of the gaseous atmosphere is recognized as an important variable and certainly more work is needed with respect to this particular incineration variable. In addition, ongoing research at the University of Dayton is involved with studying other variables and combinations of variables related to controlled high-temperature incineration.

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TABLE 1

ORGANIC COMPOUNDS ANALYZED FOR THERMAL DECOMPOSITION CHARACTERISTICS

PESTICIDES

Kepone
Mirex
p,p'-DDT
o,p'-DDT
p,p'-DDE
o,p'-DDE
Endrin
Diazinon
Hexachlorobenzene
Pentachloronitrobenzene

INDUSTRIAL MIXTURES

Polychlorinated Biphenyls
Polychlorinated Naphthalenes
Polybrominated Biphenyls
Hex Wastes
Numerous Industrial Waste Streams

PURE COMPOUNDS

Biphenyl
2,6-Dichlorobiphenyl
2,5,2',5'-Tetrachlorobiphenyl
2,5,2',4',5',-Pentachlorobiphenyl
2,4,5,2',4',5'-Hexachlorobiphenyl
Decachlorobiphenyl
2,2'-Dibromobiphenyl
Pentabromobiphenyl
2,4,5,2',4',5'-Hexachlorobiphenyl
Heptabromobiphenyl
Dibenzofuran
1,2,3,5-Tetrachlorobenzene
Pentachlorobenzene
Hexachlorobutadiene
Methane
Propane
Benzene
Acetonitrile
Acrylonitrile
Aniline
Hexachloroethane
2,8-Dichlorodibenzofuran
Dibenzo-p-dioxin
2-Chlorodibenzo-p-dioxin
2,7-Dichlorodibenzo-p-dioxin
1,2,4-Trichlorodibenzo-p-dioxin
1,2,3,4-Tetrachloronaphthalene
Heptachloronaphthalene
Triphenylene
Hexachlorocyclopentadiene
Octachlorocyclopentene
Methylene Chloride
Chloroform
Carbon Tetrachloride
Monochlorobenzene
1,2-Dichlorobenzene
1,2,4-Trichlorobenzene
Nitrobenzene
Pyridine
1,2,3,4-Tetrachlorobenzene
Tetrachloroethylene
1,1,1-Trichloroethane

TABLE 2

GAS PHASE THERMAL DECOMPOSITION VARIABLES
EXPOSURE TEMPERATURE
RESIDENCE TIME
COMPOSITION OF ATMOSPHERE
TEMPERATURE VARIATIONS
CHAMBER PRESSURE
RESIDENCE TIME DISTRIBUTION

SECTION 5

CONCEPT AND BASIC DESIGN OF TDU-GC SYSTEM

The operation and design aspects associated with the TDU-GC are similar to those of the TDAS. The sample is still inserted into the system and then gradually vaporized in a flowing carrier gas. The vaporized compounds are subsequently subjected to a controlled, high-temperature exposure. The components that emerge from the high-temperature environment are then collected and subjected to instrumental chemical analysis. (Precise quantitation is not required since data reduction employs a difference method involving the comparison of the partially decomposed sample peak size with a non-decomposed quantitation peak.) This same thermal analysis format has been employed with respect to the TDU-GC.

Figure 4 shows a block diagram of the TDU-GC, and an artist's rendering of the assembled system is presented in Figure 5. Studies can be conducted with the TDU-GC using air or any other oxygen-containing carrier. Accurate measurements of pressure and flow can be readily obtained with the TDU-GC. The internal pressure in the reactor and mass flow rate (thus mean residence time) can be continuously monitored by in-stream instrumentation.

The TDU-GC has been designed for measuring the thermal decomposition properties of a wide range of organic samples--gases, liquids, solids, and even polymers. Complicated organic mixtures can also be tested with the system by using the random entry-controlled thermal exposure (RE-CTE) process (17,19) and a slow vaporization of the sample. After vaporization, the gas

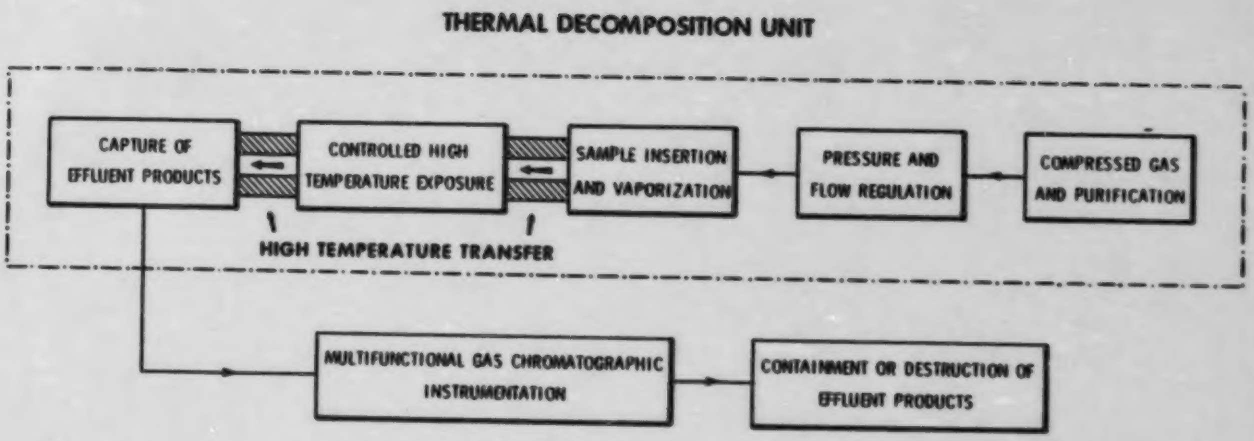

THERMAL DECOMPOSITION UNIT
CAPTURE OF EFFLUENT PRODUCTS
CONTROLLED HIGH TEMPERATURE EXPOSURE
SAMPLE INSERTION AND VAPORIZATION
PRESSURE AND FLOW REGULATION
COMPRESSED GAS AND PURIFICATION
HIGH TEMPERATURE TRANSFER
MULTIFUNCTIONAL GAS CHROMATOGRAPHIC INSTRUMENTATION
CONTAINMENT OR DESTRUCTION OF EFFLUENT PRODUCTS

Figure 4. Block Diagram of TDU-GC

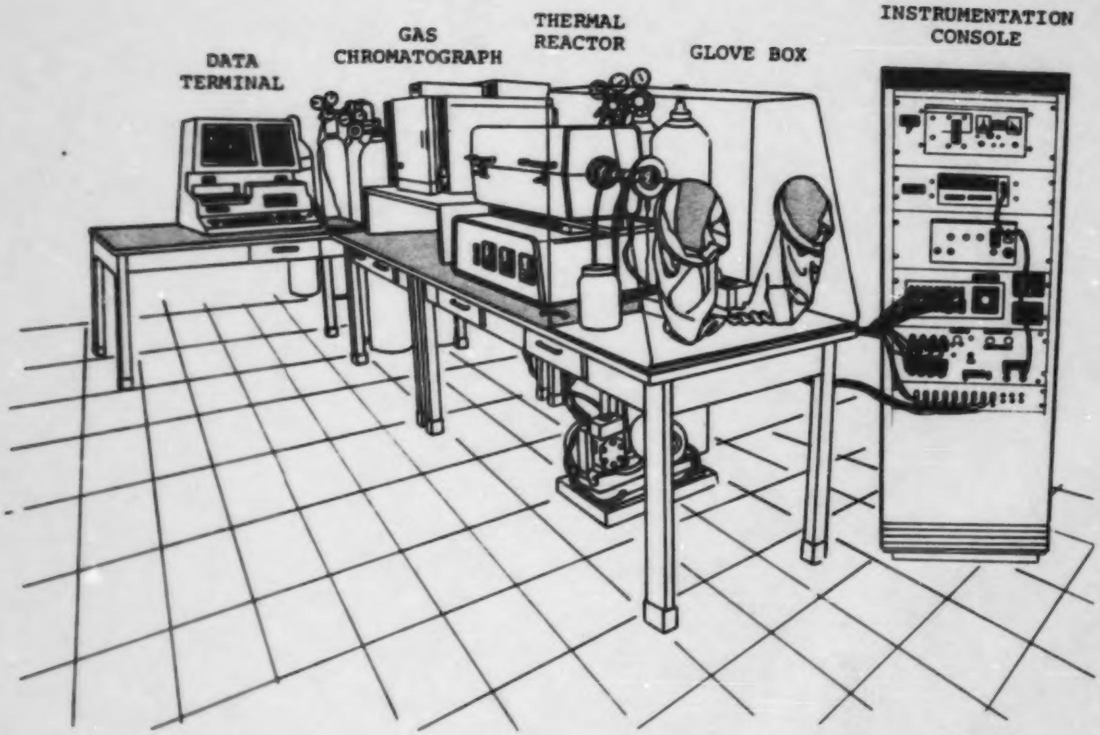

DATA
TERMINAL
GAS
CHROMATOGRAPH
THERMAL
REACTOR
GLOVE BOX
INSTRUMENTATION
CONSOLE

Figure 5. Artist's Rendering of Assembled TDU-GC.

phase molecules are subjected to precise high-temperature conditions (these range between 200°C and 1150°C and are held with ±2°C) in a fused quartz tube reactor. The emerging products are then rapidly swept into a cryogenic in-line trap where the condensable products are captured at temperatures down to minus 50°C. The collected effluent products are subsequently subjected to GC analysis using high-resolution open tubular columns. The separated compounds are then sensed by a hydrogen flame ionization detector.

The operation of the TDU-GC and the conducting of thermal decomposition tests can be accomplished with relative ease (that is, after suitable familiarization and experience). Most of the crucial instrumentation for conducting experiments with the TDU-GC have been mounted in an instrumentation console, and the test functions can be selectively monitored on this console.

The basic procedure for testing a particular sample* begins with selection of the thermal decomposition atmosphere or carrier gas. Next, the mode of sample insertion must be chosen. Then the actual exposure temperature is selected, and each of the furnace zones are set to this temperature. The next parameter to be established is the mean residence time. Once the other variables have been stabilized and measured, it is a simple matter of calculating the desired carrier flow and dialing off that value with the adjustable flow control.

---

*All samples subjected to analysis by the TDU-GC would be screened beforehand using other chromatographic instruments to verify that the sample would indeed be conducive to a TDU-GC examination.

After establishing the thermal decomposition test parameters, the next step in the procedure is to cool down the effluent collection trap so that the condensable products can be captured. The remaining steps are relatively routine. The sample must then be admitted, the products collected, and after switching to helium or nitrogen carrier gas, the captured products must be subjected to in-line analysis by high-resolution gas chromatography.

The above test procedure would yield one set of data points in the thermal decomposition procedure. Any one of the above variables could now be changed for the next thermal decomposition test, and so on, until the thermal decomposition properties of the sample are adequately characterized. Section 8 of this report presents a more detailed description of the sample preparation procedures and Section 9 provides detailed TDU-GC operation instructions.

Extensive design details covering the various TDU-GC component parts and assemblies are presented in the following sections.

SECTION 6

DESCRIPTION OF THERMAL DECOMPOSITION UNIT

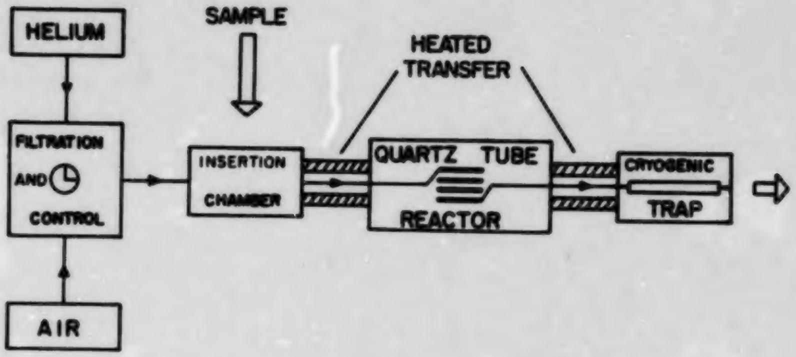
The TDU-GC is a continuous system that can be viewed as two in-line instrumental stations or units. The first unit in the system is designated as the thermal decomposition unit (TDU). Block diagrams of the TDU are shown in Figure 6. Specifically, this unit consists of the various gas supplies, an instrumentation control console, a glove-boxed compartment for sample introduction, the sample insertion chamber along with high-temperature reactor, and the various associated transfer lines. All of these components will be discussed later in this section.

The primary function of the TDU is to subject gas-phase molecules to well-defined thermal exposures. The other station of the system subsequently separates and analyzes the collected effluent compounds.

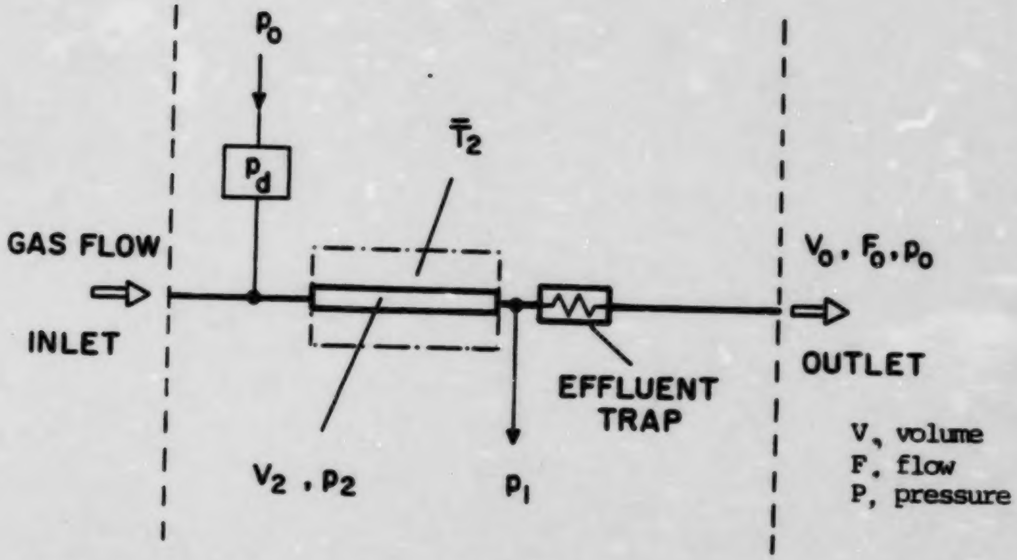
The schematic shown in Figure 6a can be redrawn as in Figure 6b to depict the physical relationships within the gas flowpath of the TDU. From this sketch, it is seen that the pressures, temperatures, and volumes can be related according to the ideal gas law as follows:

$$\frac{V_2 p_2}{\bar{T}_2} = \frac{V_o p_o}{T_o} \qquad (1)$$

where V is volume, p is pressure, T is temperature, and $\bar{T}$ is temperature averaged over the length of the reactor. The subscript 2 denotes the quartz tube interior, and the subscript o represents the ambient outlet conditions.


HELIUM
SAMPLE
HEATED TRANSFER
FILTRATION AND CONTROL
INSERTION CHAMBER
QUARTZ TUBE REACTOR
CRYOGENIC TRAP
AIR

a) BASIC SCHEMATIC


p_o
p_d
$\bar{\bar{T}}_2$
GAS FLOW
INLET
V_o, F_o, p_o
OUTLET
EFFLUENT TRAP
V_2, p_2
p_1
V, volume
F, flow
P, pressure

b) SCHEMATIC REDRAWN TO SHOW PHYSICAL RELATIONSHIPS WITHIN THE GAS FLOW PATH

Figure 6. Diagrams of the TDU.

If the impedance or resistance to gas flow presented by the downstream transfer lines R_ℓ, the in-line cryogenic trap R_t, and the restrictor R_r, is such that

$$(R_\ell + R_t + R_r) \gg R_q \tag{2}$$

where R_q represents the resistance to gas flow of the quartz tube reactor assembly, then the differential pressure p_d can be expressed as

$$p_d = p_2 - p_o = p_1 - p_o \tag{3}$$

where p_1 is the pressure at the reactor exit. Now, volumetric flow rate F can be written as

$$F = \frac{V}{t} \tag{4}$$

where t is time, and equation 1 can be rewritten as

$$\frac{V_2 p_2}{\bar{T}_2} = \frac{F_o t p_o}{T_o} \tag{5}$$

or

$$\frac{\pi r^2 L p_2}{\bar{T}_2} = \frac{F_o t p_o}{T_o} \tag{6}$$

where r and L are the tube radius and length, respectively. Therefore, it is seen that

$$\bar{t}_r = \left(\frac{\pi r^2 L}{F_o}\right)\left(\frac{T_o}{\bar{T}_2}\right)\left(1 + \frac{p_d}{p_o}\right) \tag{7}$$

where $\bar{t}_r$ represents the calculated mean residence time of a substance in the quartz tube interior.

The equipment used to measure these parameters will be discussed at length later in this section. Also, an error analysis associated with these measurement variables has been presented in an earlier study (5).

One of the distinct advantages in conducting thermal decomposition experiments using the laboratory-scale TDU-GC is that each molecule is subjected to essentially the same thermal exposure. To illustrate, consider the transport of like molecules through the high-temperature reactor. Once the sample has been admitted in the sample insertion chamber, this region is temperature programmed at a fixed rate to an elevated temperature. During this process the deposited sample would be gradually swept by the gaseous carrier from its initial location and transported as a very dilute and broad concentration profile into the high-temperature reactor of the system. However, as the pressure, temperature, and linear gas velocity within the reactor are constant, the individual molecules generate a residence time distribution as shown in Figure 7.

There are many advantages in having a Gaussian or normal residence time distribution. Linear combinations of Gaussian random variables lead to new random variables that are also Gaussian. Such simplicity is not the case for most other distribution functions. This is one of the desirable features of working with a narrow Gaussian function.

Before sample handling in the TDU is discussed, it is interesting to note from Figure 6 that both the mass flow transducer and the pressure transducer are upstream, yet in-line with the reactor and product collection trap. Therefore, with the use of these in-line sensing devices, precisely controlled thermal decomposition experiments can be conducted at subatmospheric, atmospheric, or elevated pressure.

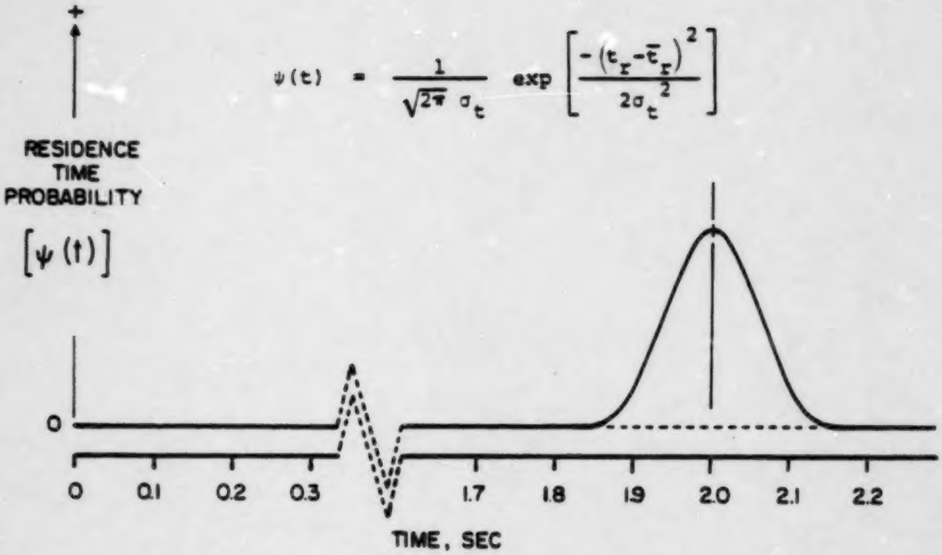


Figure 7. TDU-GC Residence Time Distribution.

Sample Handling and Insertion with the TDU-GC

The sample insertion section of the TDU-GC was designed to be as versatile as possible and there are numerous modes for inserting samples into the system. Because of the built-in flexibility (5), almost any type of organic sample can be examined.

The one major requirement with respect to sample handling with the TDU-GC is that substances leaving the sample insertion chamber must be in the gas phase. Precautions much be taken to prevent particulate material from migrating into the heated transfer lines and the high-temperature quartz tube assembly.

TDU-GC samples are either volatilized or thermally degraded in a sample insertion chamber which is shown in Figure 8. Volatilization is accomplished by controlled heating of the insertion chamber with a special temperature programmer. If sample thermal degradation is required, it can be accomplished using a variety of specially designed sample insertion devices (5) or probes (see Figures 9a through 9f). These devices can be used in the TDU-GC as the sample insertion region can be heated to high temperatures (e.g., 600°C to 700°C) whereby organic compounds can be decomposed in flow air.

The rate at which molecules are admitted into the high-temperature reactor is an important controlling factor in thermal decomposition studies. In the TDU-GC system, the sample is deposited into a fused quartz sample insertion chamber. The chamber is normally kept at room temperature and then slowly heated to 300°C by applying a controlled temperature program (e.g., 10°C min^{-1}). The sample molecules are herein thermally

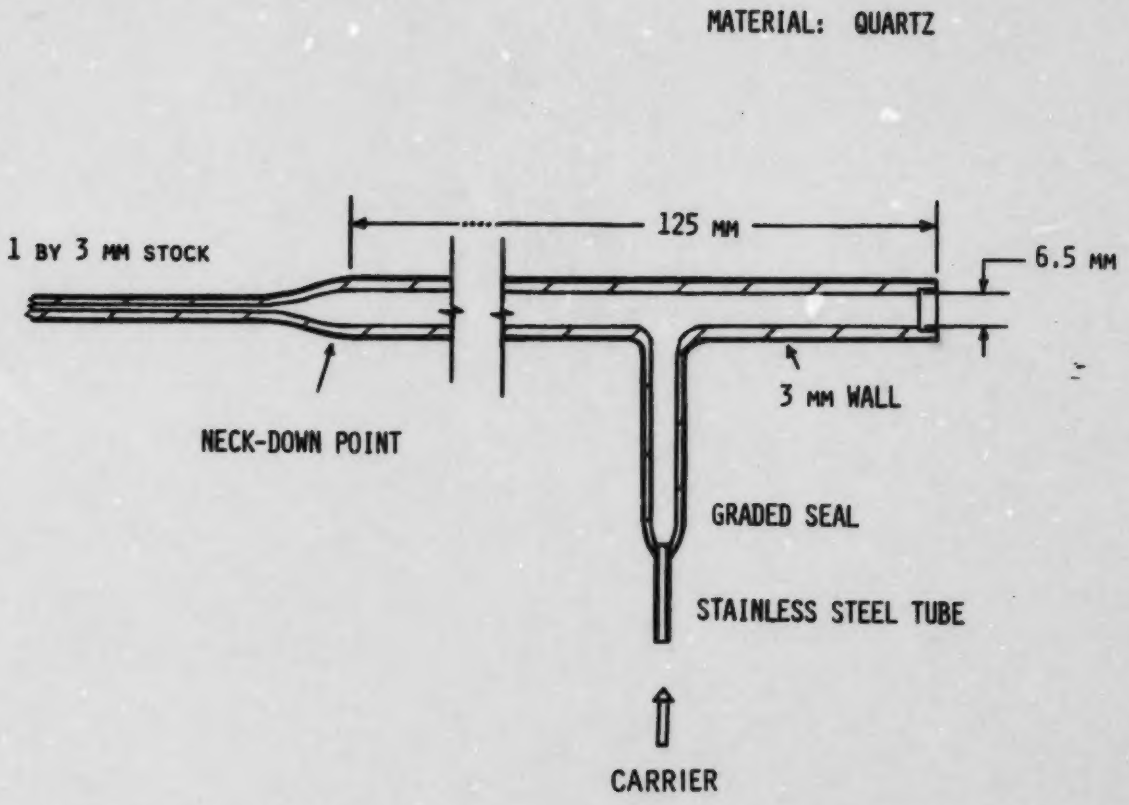

MATERIAL: QUARTZ
125 MM
1 BY 3 MM STOCK
6.5 MM
3 MM WALL
NECK-DOWN POINT
GRADED SEAL
STAINLESS STEEL TUBE
CARRIER

Figure 8. Drawing of Sample Insertion Chamber.

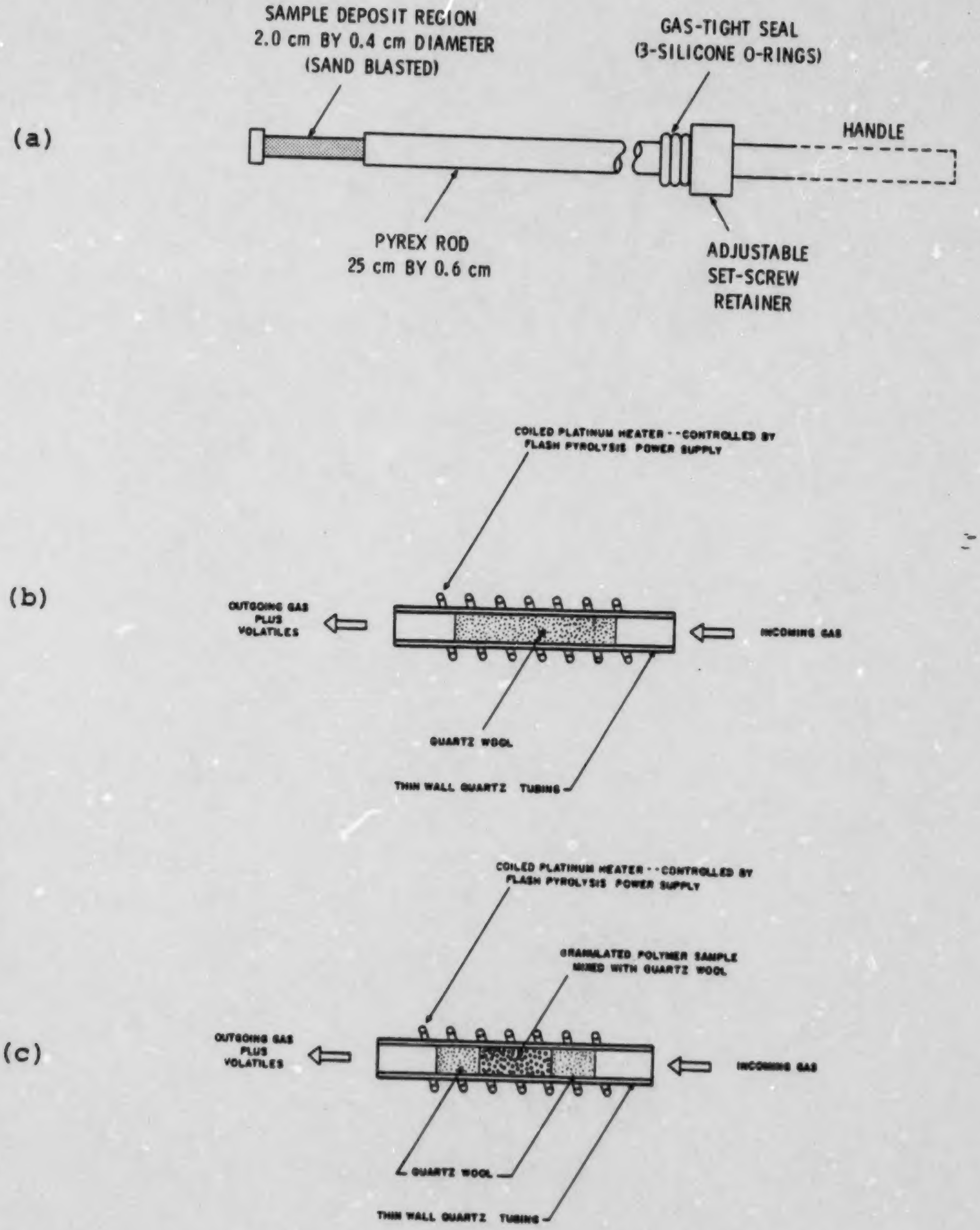

SAMPLE DEPOSIT REGION
2.0 cm BY 0.4 cm DIAMETER
(SAND BLASTED)
GAS-TIGHT SEAL
(3-SILICONE O-RINGS)
(a)
HANDLE
PYREX ROD
25 cm BY 0.6 cm
ADJUSTABLE
SET-SCREW
RETAINER
COILED PLATINUM HEATER --CONTROLLED BY
FLASH PYROLYSIS POWER SUPPLY
(b)
OUTGOING GAS
PLUS
VOLATILES
INCOMING GAS
QUARTZ WOOL
THIN WALL QUARTZ TUBING
COILED PLATINUM HEATER --CONTROLLED BY
FLASH PYROLYSIS POWER SUPPLY
GRANULATED POLYMER SAMPLE
MIXED WITH QUARTZ WOOL
(c)
OUTGOING GAS
PLUS
VOLATILES
INCOMING GAS
QUARTZ WOOL
THIN WALL QUARTZ TUBING

Figure 9. Various Sample Insertion Probes.

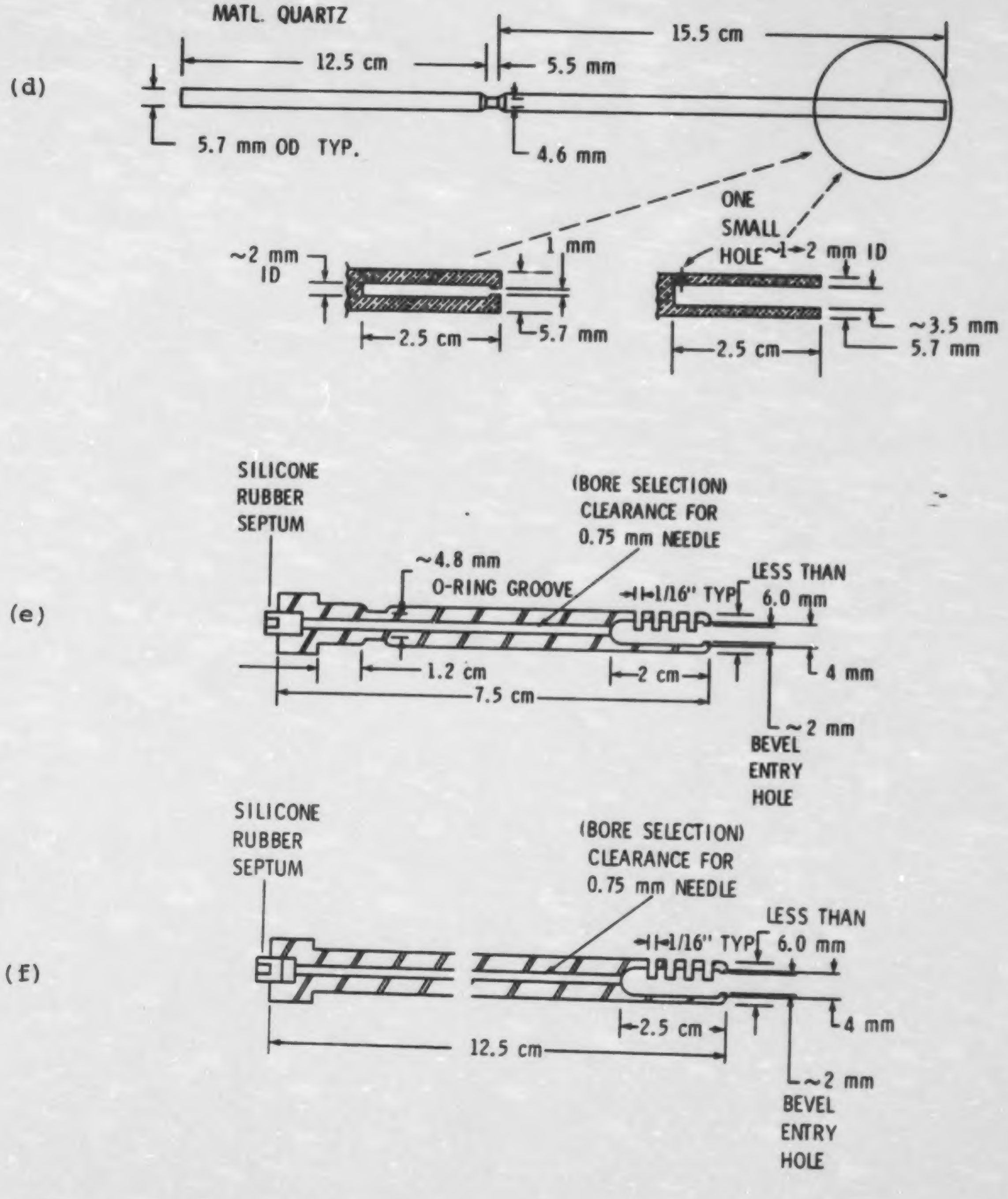

(d)
MATL. QUARTZ
12.5 cm
15.5 cm
5.5 mm
5.7 mm OD TYP.
4.6 mm
ONE
SMALL
HOLE
~1→2 mm ID
~2 mm
ID
1 mm
5.7 mm
2.5 cm
2.5 cm
~3.5 mm
5.7 mm
(e)
SILICONE
RUBBER
SEPTUM
(BORE SELECTION)
CLEARANCE FOR
0.75 mm NEEDLE
~4.8 mm
O-RING GROOVE
1/16" TYP
LESS THAN
6.0 mm
1.2 cm
2 cm
7.5 cm
4 mm
~2 mm
BEVEL
ENTRY
HOLE
(f)
SILICONE
RUBBER
SEPTUM
(BORE SELECTION)
CLEARANCE FOR
0.75 mm NEEDLE
1/16" TYP
LESS THAN
6.0 mm
2.5 cm
12.5 cm
4 mm
~2 mm
BEVEL
ENTRY
HOLE

Figure 9. (Continued) Various Sample Insertion Probes.

desorbed and theoretically are exposed to virtually the same thermal environment.

The sample insertion section of the TDU-GC system is contained in a Plexiglass glove box (Figure 10). The inlet of the fused quartz tubular reactor assembly is connected to a 1.0 mm ID quartz tube to which the sample insertion chamber is attached. The chamber accommodates a variety of sample insertion devices and probes. One insertion device consists of a fused quartz tube that allows the insertion of a chromatographic syringe needle through a septum receptacle on one end. Schematics of this type of sample insertion probe are presented in Figures 9e and 9f.

As seen in Figure 9, the downstream end of this particular insertion device consists of a cavity with slits in the wall for transport gas access and containment of loosely packed quartz wool. The quartz wool packing serves two purposes. The sample is deposited into the quartz wool at room temperature, as mentioned before, and is temporarily retained until heat is applied. In addition, the quartz wool serves to wipe the syringe needle clean of any remaining sample as the syringe needle is withdrawn from the injection insert.

The 1.0 mm ID tubing downstream of the insertion chamber is surrounded by an outer quartz tube jacket. There are a number of heating elements located on the outer diameter of the insertion assembly which are controlled by a temperature programmer (Theall Engineering, TP-2000-T8X-R2-P1-S6) located in the instrumentation console. Using a flow of heat transfer air and auxillary heaters,

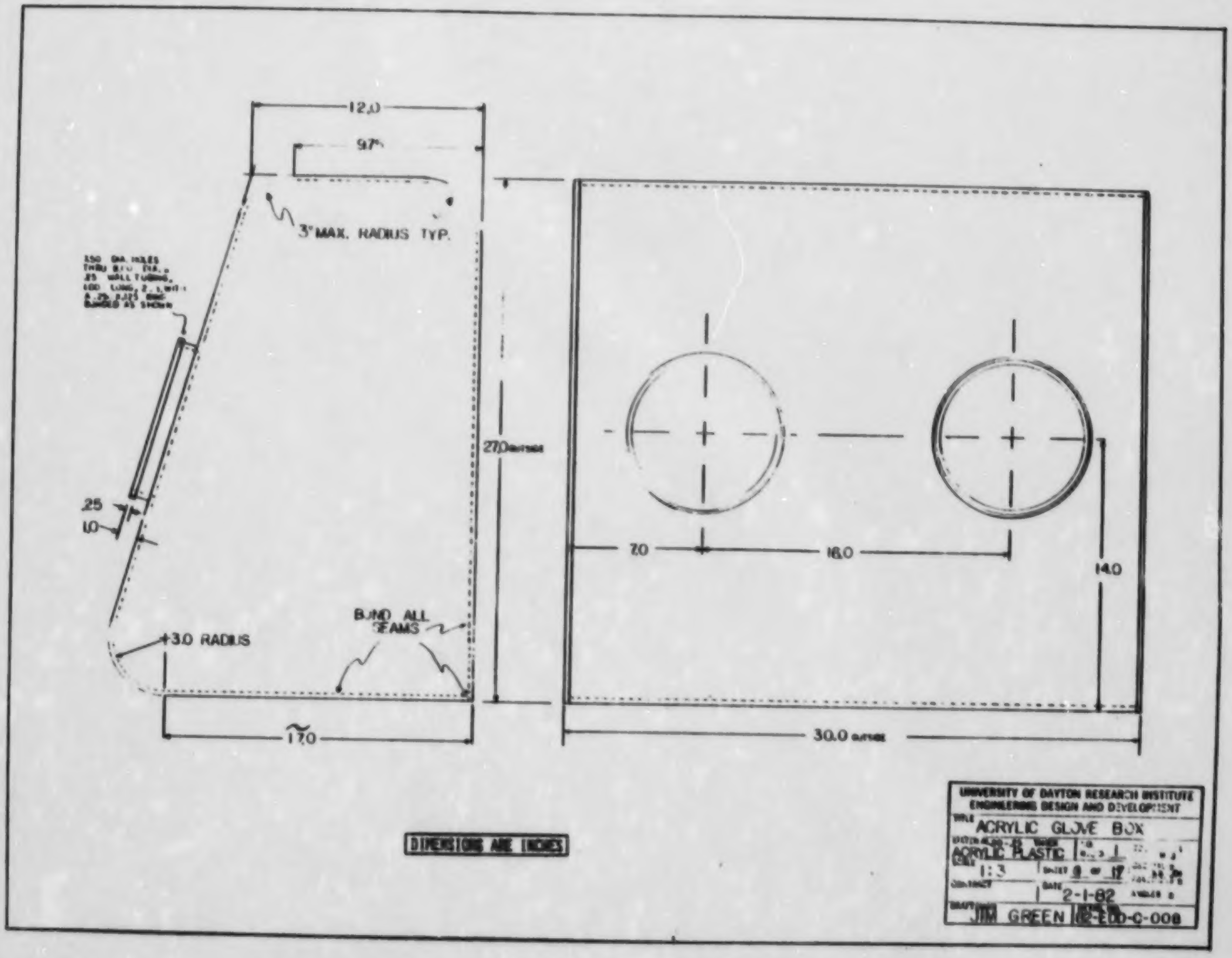

12.0
9.7
3" MAX. RADIUS TYP.
.25
1.0
+3.0 RADIUS
BOND ALL SEAMS
17.0
27.0
7.0
18.0
14.0
30.0
DIMENSIONS ARE INCHES
UNIVERSITY OF DAYTON RESEARCH INSTITUTE
ENGINEERING DESIGN AND DEVELOPMENT
ACRYLIC GLOVE BOX
ACRYLIC PLASTIC
1:3
2-1-82
JIM GREEN
82-EDD-C-008

Figure 10. Engineering Drawing of Glove Box.

a uniform temperature distribution is obtained for transporting the gas-phase sample from the insertion point to the reactor assembly.

Transport of Sample and Effluent Products in the TDU-GC

Three basic criteria must be met for proper transport of gas-phase samples. First, the transport tubing material must not interact with any of the chemical substances that constitute the flowing media. Second, it is important that a constant flow of sweeping gas be maintained throughout every portion of the transport path. Third, the gas transfer must be maintained at elevated temperatures that are compatible with the flowing media. Each of these criteria require some elaboration relative to the transport of sample and products in the TDU-GC.

Fused quartz was used as the tubing material for sample transport in the TDU-GC. However, a Nickel 200 transfer line was required for sample that was passed on to a preparative collection trap.

The second basic requirement for good transport of sample involves the continual gas sweeping of the transfer tubing. It is desirable that the transport gas flow be maintained at relatively high linear velocities (that is, greater than 20 cm sec^{-1}). Thus the inside diameter of the transport tube should be relatively small, e.g., less than 1.0 mm ID. Unswept recesses in a gas flowpath can present major transport problems. Consequently, tubing transitions should be minimized.

The selection of transport temperature and the maintenance of uniform temperature along the transport path, constitutes the third criteria for proper transfer of sample. The selected transport temperature must be high enough to avoid any serious condensation and possible adsorption effects. However, it must be low enough that additional gas-phase reactions do not occur during transport. Localized cold or hot regions must be avoided.

The transfer tubing used in the TDU-GC was jacketed with insulation and then wrapped with special heating tape. The outer diameters were first instrumented with thermocouples located at key positions along the tube. The thermocouples were attached to the outer tube with the use of glass adhesive tape (3M Company, No. 27 tape). After electrically insulating the various conductors along the transport line with woven glass or quartz tape (Ware Apparatus Co., 1701 and 1790, respective), the tubular assembly was wrapped with high-temperature heating tape (flexible Samox fiber tape from Thermolyne Corp., BW0041-020). The heating tape was then wrapped with another layer of woven quartz tape. Table 3 shows the various thermocouple locations and their corresponding maximum temperatures for gas transport in the TDU-GC.

During the course of conducting experiments with the TDU-GC, certain vital components in the transport path are intentionally cooled to very low temperatures. This localized cooling is necessary to retain the products emerging from the TDU. Details concerning this low temperature procedure will be discussed later in this section.

TABLE 3

TDU TEMPERATURES

Temperature Selector Position	Thermocouple Location	Maximum Temperature (°C)
1	Room temperature (tc in connector)	30
2	Sample insertion region	600
3	Pre-reactor transfer tube	500
4	Mid point of inlet heat transfer cavity	600
5	Reactor end region of inlet cavity	600
6	Reactor end region of outlet cavity	600
7	Mid point of outlet heat transfer cavity	600
8	Junction of glass-lined and quart tubing	400
9	Transfer tubing upstream of collection trap	300

Quartz Tubular Reactor Assembly

One of the most important components of the TDU-GC system is the high-temperature reactor. The design and performance of the high-temperature reactor is vitally important to the entire TDU-GC. Consequently, considerable attention has been centered upon this component. As stated earlier, the important thermal decomposition variables encountered thus far (i.e., gas-phase environment, mean residence time and distribution profile, exposure temperature, variations in temperature, and pressure) apply directly to the interior of the reactor.

The design considerations and details of the thermal reactor and its assembly are found in a previous report on the development of the TDAS (5). The major portion of the reactor consists of a narrow-bore nominal 1.0 mm ID quartz tubular flowpath in a race-track configuration (3.5 cycles, 1 meter in length). This reactor was specially fabricated using high-purity fused quartz tubing obtained from Heraeus-Amersil, Inc. This material and construction minimizes the possibility of wall reactions while simultaneously providing a very narrow residence time distribution and square-wave exposure temperature profile. In addiiton, the reactor design has very fine bore entrance and exit tubes to transport the sample rapidly into and out of the central portion of the reactor. Tubing internal diameter measurements were obtained using the mercury displacement technique. Details of the quartz tube reactor are given in Figure 11.

The multiple fold design of the race-track reactor assures that sample molecules encounter essentially isothermal conditions

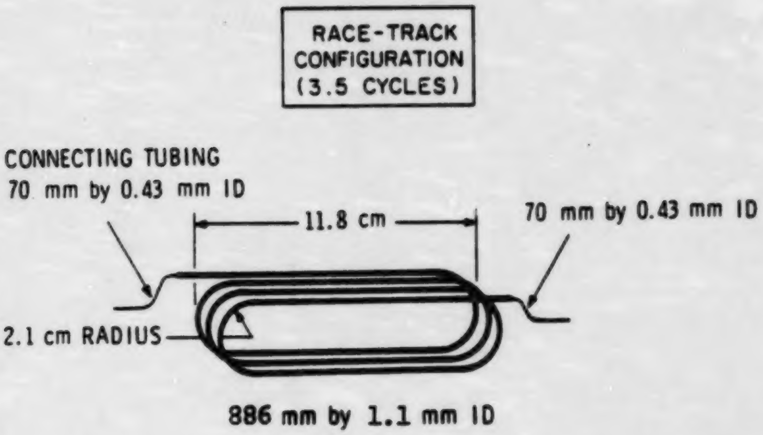

RACE-TRACK
CONFIGURATION
(3.5 CYCLES)
CONNECTING TUBING
70 mm by 0.43 mm ID
11.8 cm
70 mm by 0.43 mm ID
2.1 cm RADIUS
886 mm by 1.1 mm ID

Figure 11. Detail of Quartz Tube Reactor.

during their traverse through the reactor due to the averaging of the existing subtle longitudinal temperature gradients. In addition, there is a very low pressure drop across the reactor even at high-linear gas velocities. The average residence time of molecules that have passed through the reactor can be accurately calculated from the measured experimental parameters.

The furnace selected for heating this quartz assembly was a Lindberg Model 54357, a three-zone furnace of hinged construction that was designed for continuous operation at temperatures up to 1200°C. This furnace has its own control console (Model 59744-A) which separately regulates the temperatures of each of the three zones. The middle portion of the furnace is used to heat the high-temperature reactor, although during operation each of the three zones of the Lindberg furnace is held under isothermal conditions. Figure 12 shows a sectional view of the furnace interior along with the locations of the thermocouples used for controlling temperatures within the three separate zones (see Appendices for further details of furnace components).

The assembled quartzware which was eventually positioned in the high-temperature furnace is detailed in Figure 13. This quartzware, and all of the other glass and quartzware employed in the TDU-GC, was fabricated in the University Glass Shop by a scientific glassblower. Even though the assembled quartzware is delicate, it has experienced considerable use at extreme temperatures without problems.

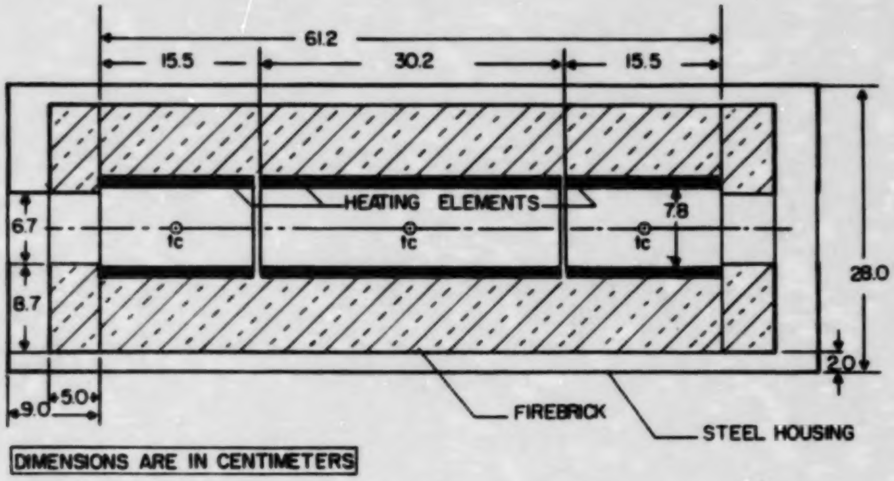

61.2
15.5
30.2
15.5
HEATING ELEMENTS
7.8
6.7
tc
tc
tc
28.0
8.7
2.0
9.0
5.0
FIREBRICK
STEEL HOUSING
DIMENSIONS ARE IN CENTIMETERS

Figure 12. Sectional View of Furnace Interior.

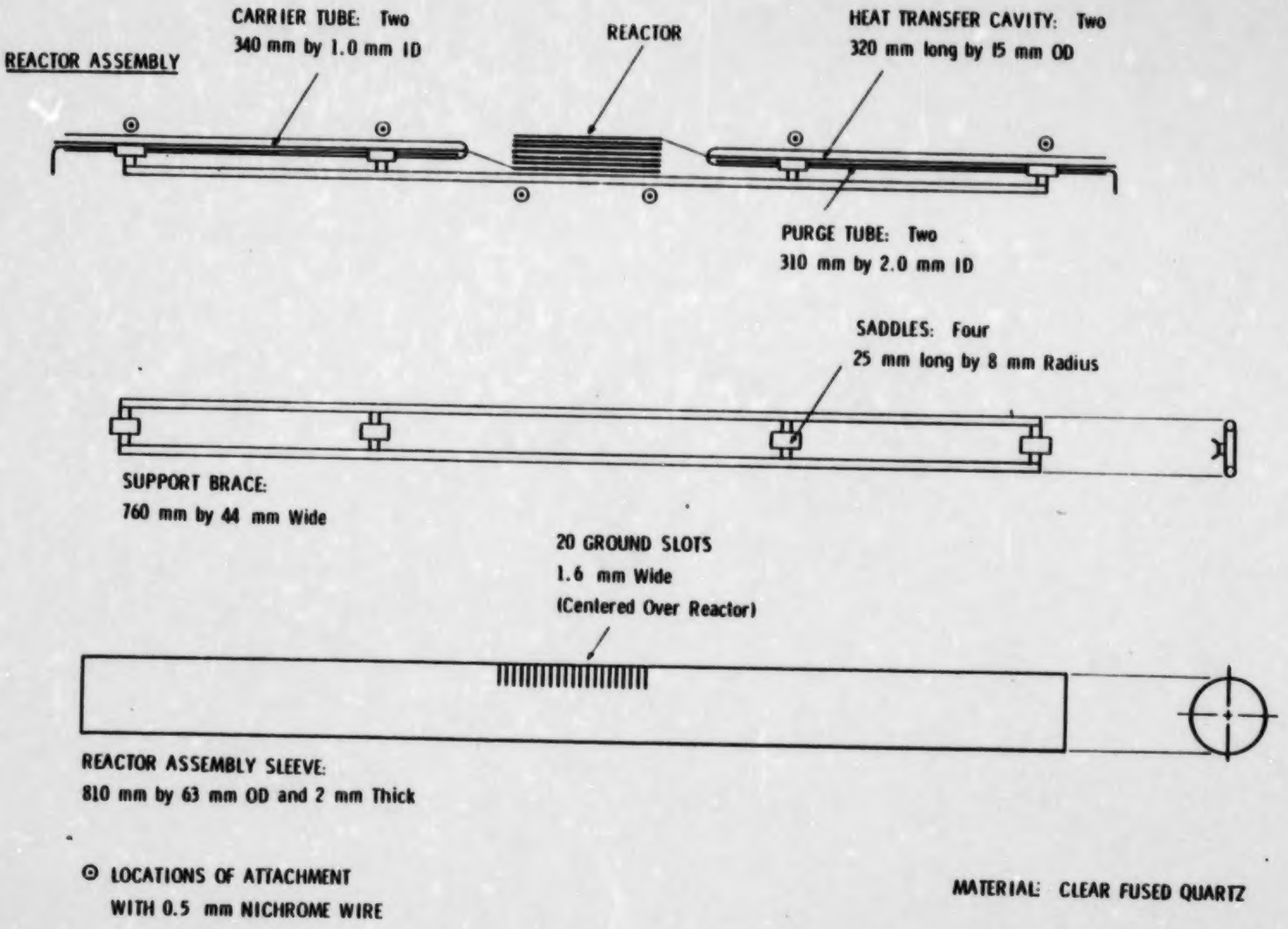
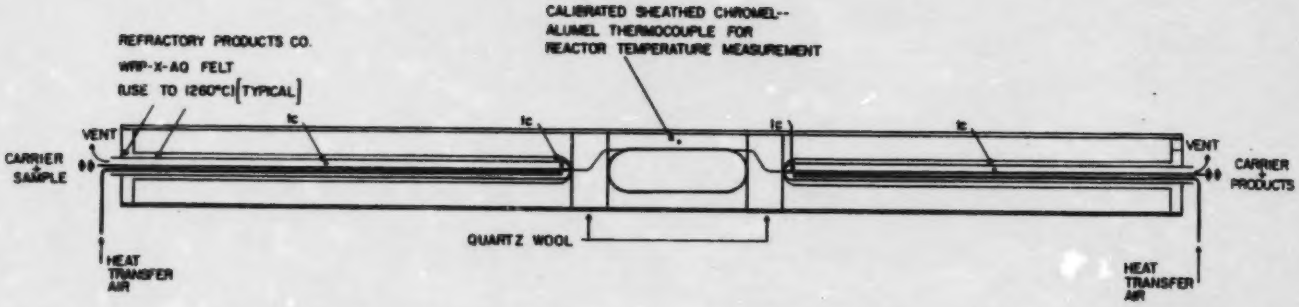

REACTOR ASSEMBLY
CARRIER TUBE: Two
340 mm by 1.0 mm ID
REACTOR
HEAT TRANSFER CAVITY: Two
320 mm long by 15 mm OD
PURGE TUBE: Two
310 mm by 2.0 mm ID
SADDLES: Four
25 mm long by 8 mm Radius
SUPPORT BRACE:
760 mm by 44 mm Wide
20 GROUND SLOTS
1.6 mm Wide
(Centered Over Reactor)
REACTOR ASSEMBLY SLEEVE:
810 mm by 63 mm OD and 2 mm Thick
⊙ LOCATIONS OF ATTACHMENT
WITH 0.5 mm NICHROME WIRE
MATERIAL: CLEAR FUSED QUARTZ

Figure 13. Quartz Tube Reactor Components.

A better understanding of the actual behavior of the entire quartz tube assembly can be obtained by close inspection of the schematic shown in Figure 14 . In this figure, three separate gas flow paths are depicted. The main flow is the carrier stream through the transfer tubing, into the reactor, and out the exit transfer tubing. This gas flowpath carries the vaporized sample molecules into the reactor, where they are subjected to the controlled high-temperature conditions and then passed downstream where the various products are collected and eventually subjected to analysis. The other two gas flowpaths consist of adjustable flows of heat transfer air that cool the entrance and exit chambers of the quartz tube assembly. Thus the main gas flow into the reactor is maintained at lower nondestructive temperatures right up to the point of entry into the high-temperature reactor. As soon as the sample or product molecules leave the reactor, the gas temperature is abruptly decreased to the same nondestruction transport level (approximately 275°C). The gas then flows on to the cryogenic collection in the GC oven at approximately the same temperature. Figure 15 shows the quartzware assembly centrally located in the three-zone furnace.

In the TDU-GC design, gas-phase molecules are subjected to a narrow residence time distribution. The design of this quartz tube reactor permits a detailed description of gas flow behavior within the reactor. Such a detailed analysis is presented elsewhere (5).



CALIBRATED SHEATHED CHROMEL--
ALUMEL THERMOCOUPLE FOR
REACTOR TEMPERATURE MEASUREMENT
REFRACTORY PRODUCTS CO.
WRP-X-AQ FELT
(USE TO 1260°C)[TYPICAL]
VENT
tc
tc
tc
tc
VENT
CARRIER + SAMPLE
CARRIER + PRODUCTS
QUARTZ WOOL
HEAT TRANSFER AIR
HEAT TRANSFER AIR

Figure 14. Assembled Quartzware.

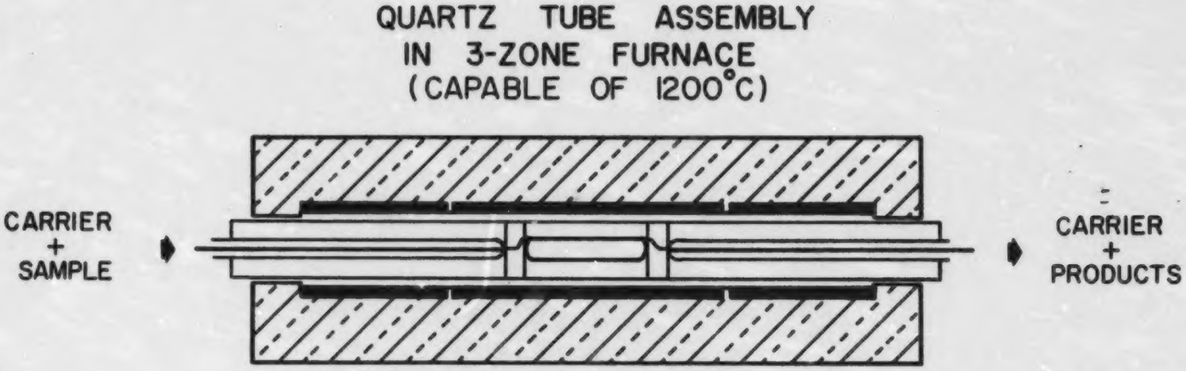

QUARTZ TUBE ASSEMBLY
IN 3-ZONE FURNACE
(CAPABLE OF 1200°C)
CARRIER
+
SAMPLE
CARRIER
+
PRODUCTS

Figure 15. Quartzware Assembly in Three-Zone Furnace.

Additional details concerning the high-temperature gas flow into and out of the quartz tube reactor are illustrated in Figure 16. Basically, this design permits negligible flowpath end effects and entrance length distortions. The steady state heat transfer effects for this reactor have been studied (5), and a very rapid temperature transition time was found for molecules passing through the quartz tube reactor. Specifically, Figure 17 shows the incoming gas reaching the elevated temperature in less than 5 milliseconds. This essentially square-wave profile of temperature versus time is accomplished through the use of the low-temperature heat transfer principle whereby the incoming gas is maintained at transport temperatures right up to the point of entry into the high-temperature region. Then by employing fine-bore connecting tubes, the linear gas velocity is dramatically increased at the entrance and also quickly reduced at the exit of the high-temperature reactor.

This high-temperature quarts tube reactor is capable of withstanding intense temperatures for long periods of time. However, it can be easily damaged by some corrosive gases. Consequently, care must be exercised with respect to determining what samples are to be subjected to analysis by the TDU-GC. If indeed the surface of the quartz tube is attacked, and increased surface area and adsorptive behavior result, then the precise residence time control no longer applies. A certain amount of sample screening* is necessary before an unknown sample can be subjected to thermal decomposition analysis by the TDU-GC.

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*See footnote on page 18.

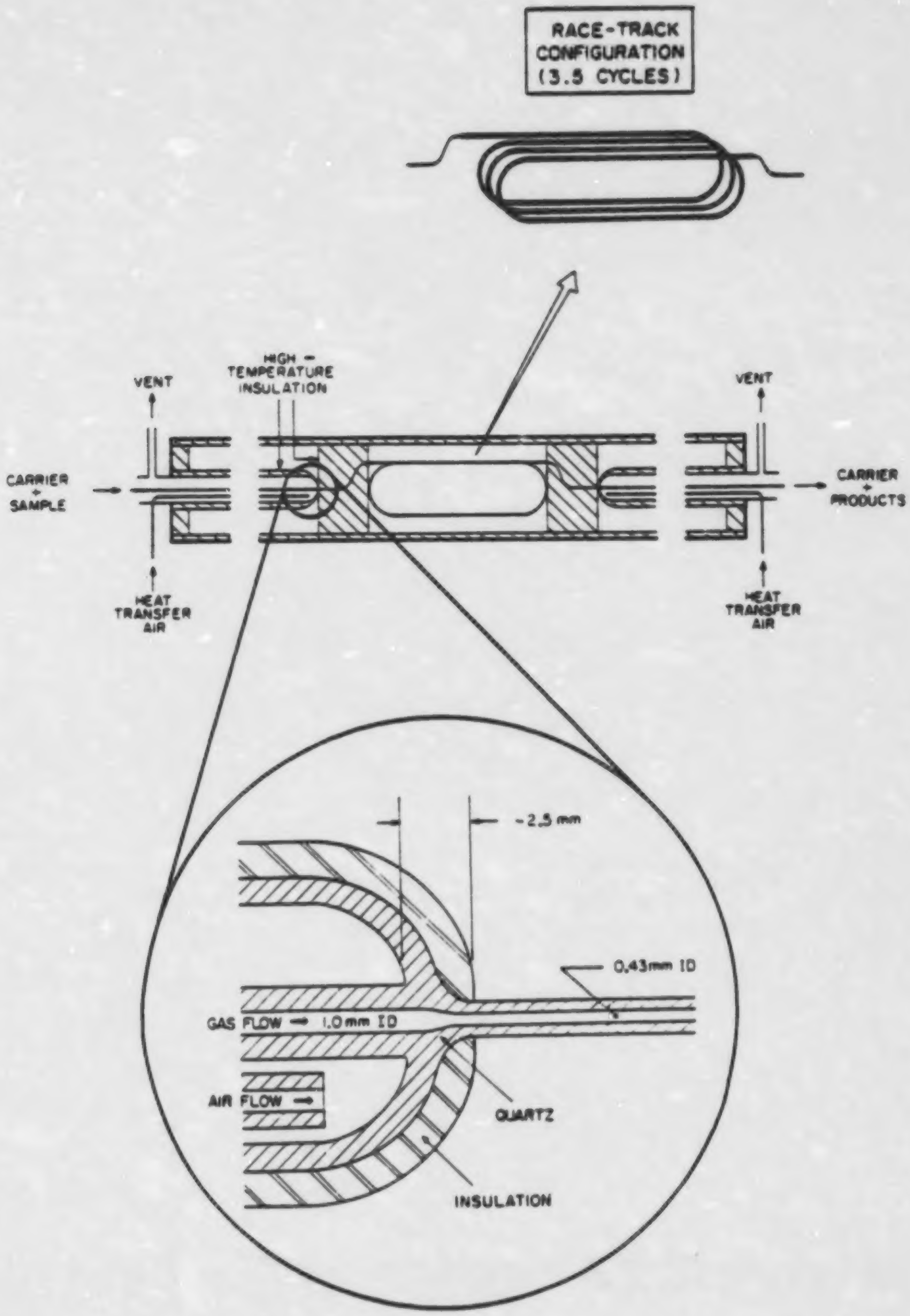
RACE-TRACK CONFIGURATION (3.5 CYCLES)
HIGH-TEMPERATURE INSULATION
VENT
VENT
CARRIER + SAMPLE
CARRIER + PRODUCTS
HEAT TRANSFER AIR
HEAT TRANSFER AIR
~2.5 mm
0.43mm ID
GAS FLOW → 1.0mm ID
AIR FLOW →
QUARTZ
INSULATION

Figure 16. Additional Details of Reactor Assembly.

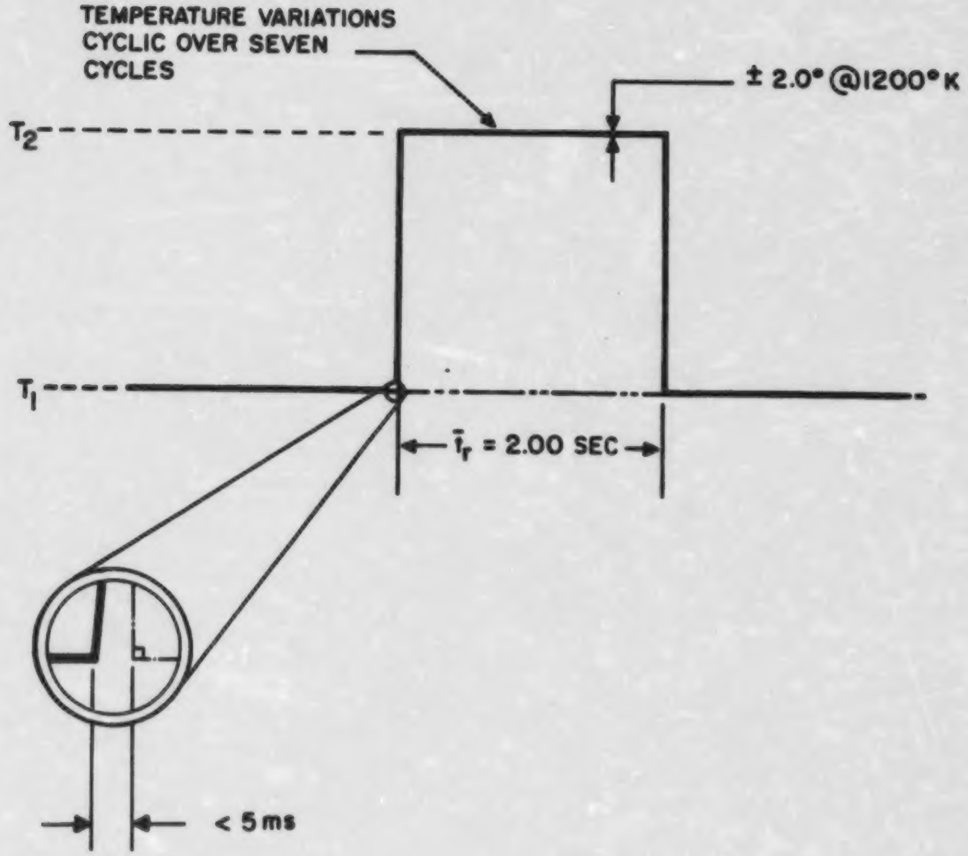
TEMPERATURE VARIATIONS CYCLIC OVER SEVEN CYCLES
± 2.0° @1200° K
T_2
T_1
$\bar{t}_r$ = 2.00 SEC
< 5 ms

Figure 17. Square Wave Profile of Gas-Phase Temperature Versus Time.

Collection of TDU Effluent Products

The primary function of the effluent collection trap is to quantitatively capture the unreacted sample and the various products of thermal decomposition that emerge from the high-temperature reactor. Therefore, as the gas phase sample and its various decomposition products emerge from the high-temperature reactor, they are swept downstream through the heated transfer line and into the effluent product collection trap. This product collection trap is an important component in the TDU-GC system and requires considerable discussion.

The utilization of collection traps at cryogenic temperatures has been in practice for many years in the field of gas chromatography (20). Indeed, the benefits of low-temperature trapping of samples are well known. However, there are also numerous problems associated with low-temperature condensing traps. One of the major difficulties is that of the condensing out of very large quantities of water along with the various organic compounds of interest.

Many procedures have been developed for thermally desorbing collection traps, including cryogenic sample collections (21,22). Some of these techniques can liberate the captured sample in a very short period of time. It can then be passed downstream into either a chromatograph or some other analytical instrument.

In the TDU-GC, the effluent from the high-temperature reactor is swept through the heated exit transfer line and into the gas chromatograph. Before reaching the inlet of the capillary column, a 30:1 split occurs in a specially designed interface (see Figure 18) and only a small portion (~3%) of the effluent sample passes on to the column. The larger portion of the sample is diverted through an activated charcoal trap and then the carrier is vented to the atmosphere. This effluent splitting is necessary to prevent overloading of the GC open tubular column (OTC).

Instrumentation Associated with the TDU

The assembled TDU-GC system includes a versatile modular instrumentation console which is used to monitor and control the many experimental variables, such as reactor temperature, gas flow rate, transport temperatures, pressure, etc. A drawing of this instrumentation console is presented in Figure 19, along with the descriptive designations of the modules that measure or control the various operations performed by the TDU. These modules are mounted in a modular electronic cabinet assembly (Cabtron Systems, Inc., AFCB-1952-25).

The temperature programming function for the sample insertion process is accomplished with the use of a Theall Engineering (TP-2000-T8X-R2-P1-S6) temperature programmer. This device is capable of generating linear temperature programs from minus 150° to plus 700°C. The mass flow and pressure readout module consists essentially of a Fluke 8030A digital multimeter. The signal output from the mass flow transducer is in the range of volts DC, whereas the output from the differential pressure transducer is read out in millivolts DC.

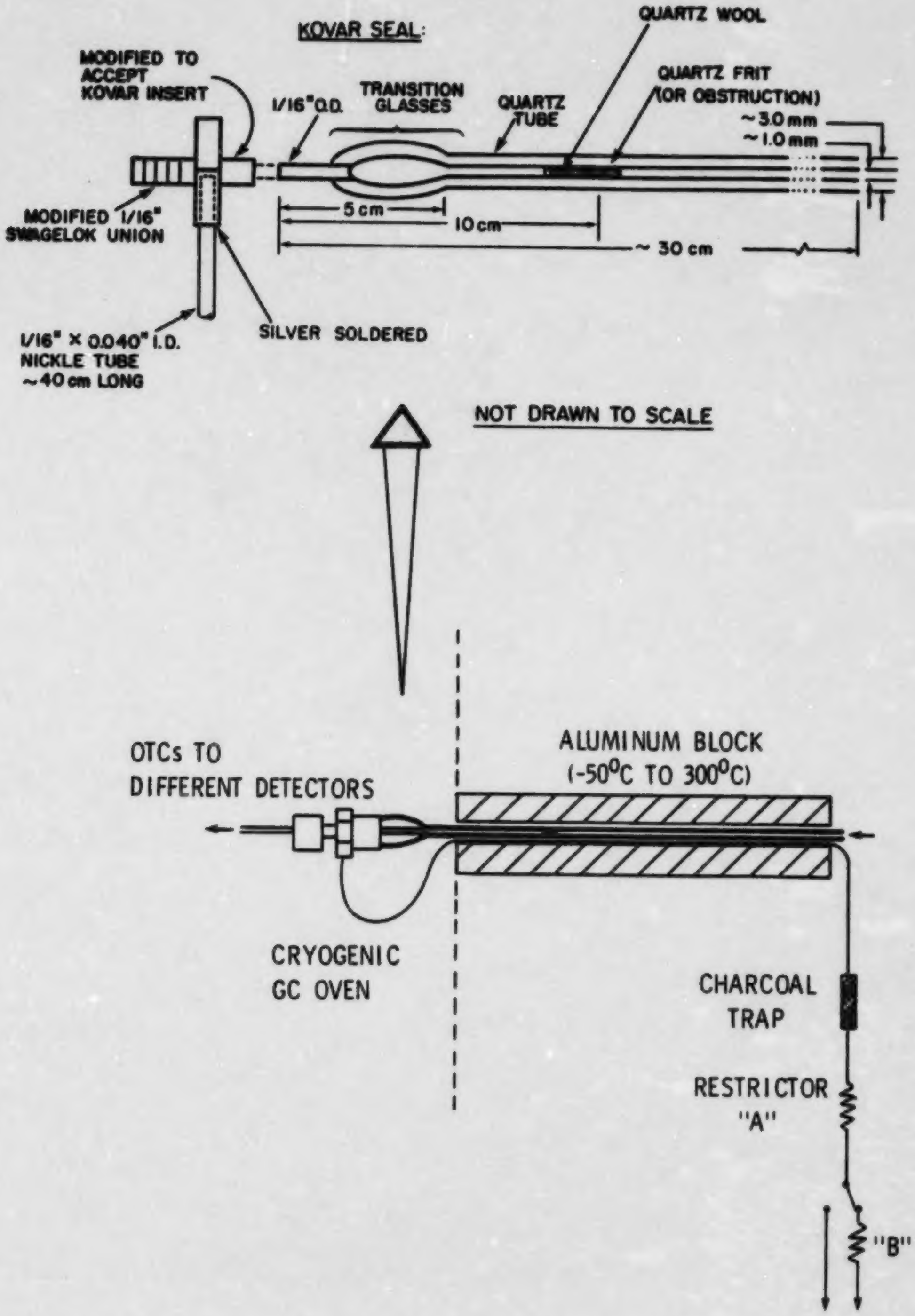
KOVAR SEAL:
QUARTZ WOOL
MODIFIED TO ACCEPT KOVAR INSERT
QUARTZ FRIT (OR OBSTRUCTION)
1/16" O.D.
TRANSITION GLASSES
QUARTZ TUBE
~3.0 mm
~1.0 mm
MODIFIED 1/16" SWAGELOK UNION
5 cm
10 cm
~ 30 cm
1/16" × 0.040" I.D. NICKLE TUBE ~40 cm LONG
SILVER SOLDERED
NOT DRAWN TO SCALE
OTCs TO DIFFERENT DETECTORS
ALUMINUM BLOCK (-50°C TO 300°C)
CRYOGENIC GC OVEN
CHARCOAL TRAP
RESTRICTOR "A"
"B"

Figure 18. Schematic of Interface and Cyrogenic Trap.

Reproduced from
best available copy.

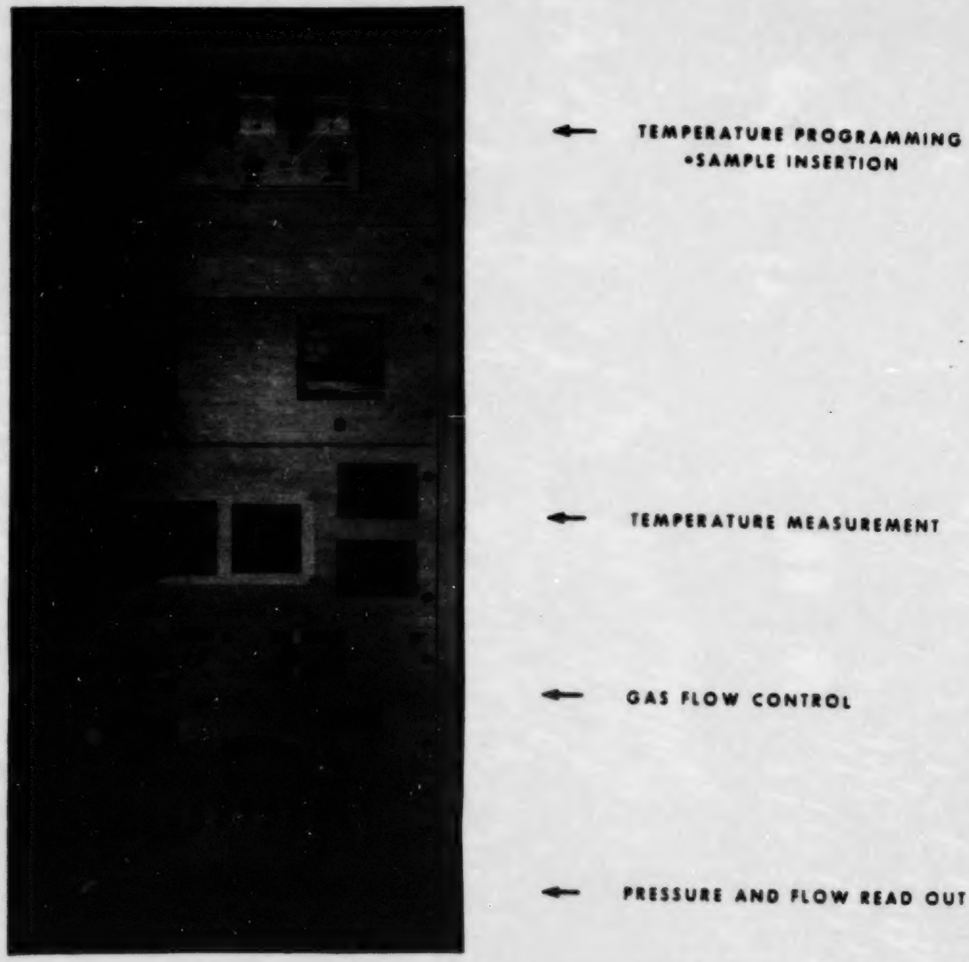
TEMPERATURE PROGRAMMING
•SAMPLE INSERTION
TEMPERATURE MEASUREMENT
GAS FLOW CONTROL
PRESSURE AND FLOW READ OUT

Figure 19. TDU Console and Instrumentation Modules.

The temperature measurement module consists of 18 Chromel-Alumel thermocouple inputs, a thermocouple selector switch (Omega MTG-OSW3-18), and two digital temperature indicators (Omega 199 KC-X-X and Omega 2160 K). The average temperature of the quartz tube reactor is continually monitored by the Omega 2160K. The temperature of the reactor, the various heated transfer lines, and the inlet assembly can be continuously monitored and adjusted from the instrumentation console.

The gas flow control module contains the various gas input connections, a carrier gas filter (Applied Science Laboratory, 14503 Hydro-Purge), a gas switching valve (Carle Instruments, 5611), needle valves (Nupro, B-4MA) that control the flow of heat transfer air in the high-temperature reactor assembly, the variable flow controller (Porter Instruments, VCD 1000, A-60) that controls the actual gas flow to the reactor, and the flow and pressure transducers along with their associated electronics.

Because of its direct interaction with the high-temperature reactor, the gas flow control module is a very important system component. A photograph of the interior of this isolated module is presented in Figure 20. (Notice the positioning of the mass flow and differential pressure sensing elements relative to the thermometer, or thermocouple, and the mounted circular level).

The principle behind the operation of the mass flow meter is well established. Although there are numerous different methods for measuring in-line gas flow, this particular flow measurement device has performed quite well in laboratory studies where

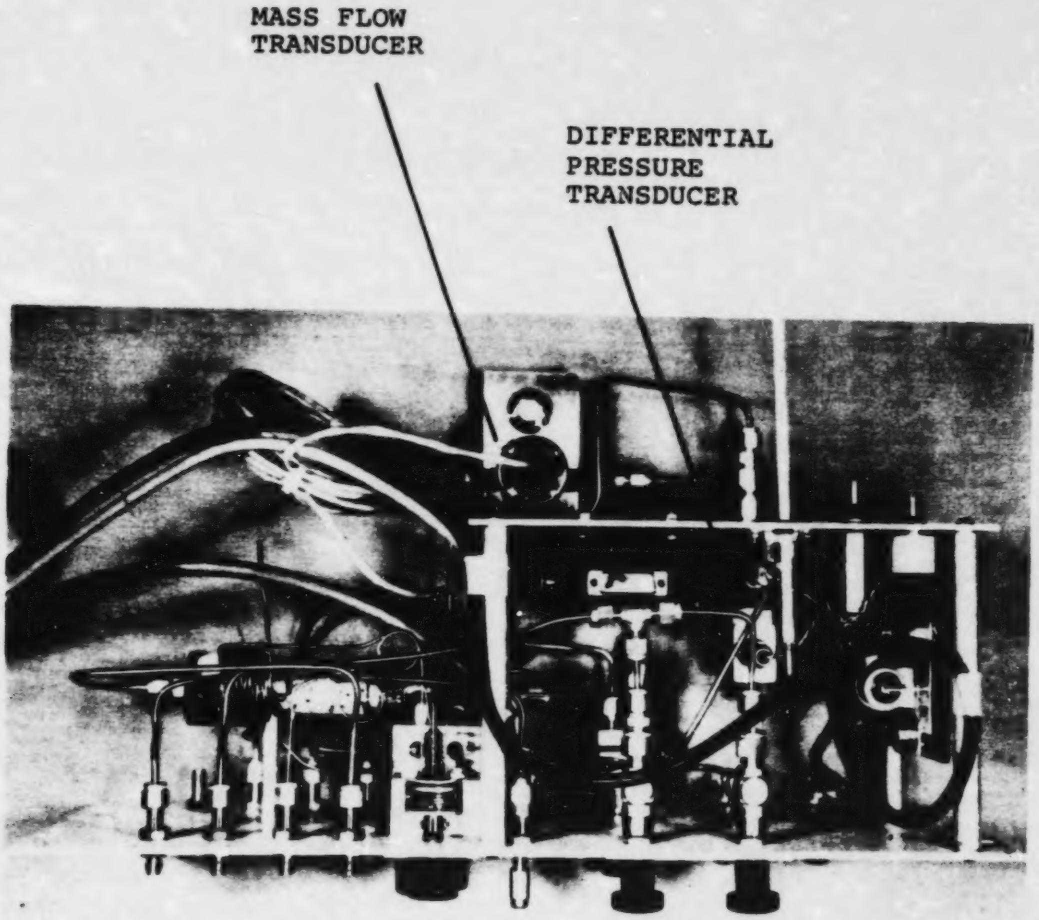
MASS FLOW
TRANSDUCER
DIFFERENTIAL
PRESSURE
TRANSDUCER

Figure 20. Interior of Gas Flow Control Module.

accurate measurements of in-line gas flow were required. A schematic showing the principle of operation of the mass flow transducer and the simplified associated electronic circuitry is shown in Figure 21. Also, a schematic drawing of the pressure transducer used in the module is shown in Figure 22. Both of these transducers have a fixed working range. The mass flow transducer is calibrated to handle flows of air up to 50 cm^3min^{-1}, and the differential pressure transducer is designed for use up to 2.0 absolute atmospheres. Each of these sensitive components has a built-in safety factor that allows them to handle somewhat higher gas flows and pressures. However, the recommended upper values are as stated above. If TDU-GC work is anticipated at flows and pressure beyond these limits, different transducers would have to be substituted.

Calibrations of the various measurement components housed in the instrumentation console were performed using methods described in Appendix D of reference 5.

Two additional measurements are routinely made in the course of conducting a test with the TDU-GC. One of these measurements is ambient temperature. This temperature measurement is made with a thermocouple which is located in the vicinity of the pressure transducer. The other important measurement is that of barometric pressure, and this measurement is taken using a Sargent-Welch S-4565 vernier rack barometer, which reads the height of a mercury column to the nearest 0.1mm.

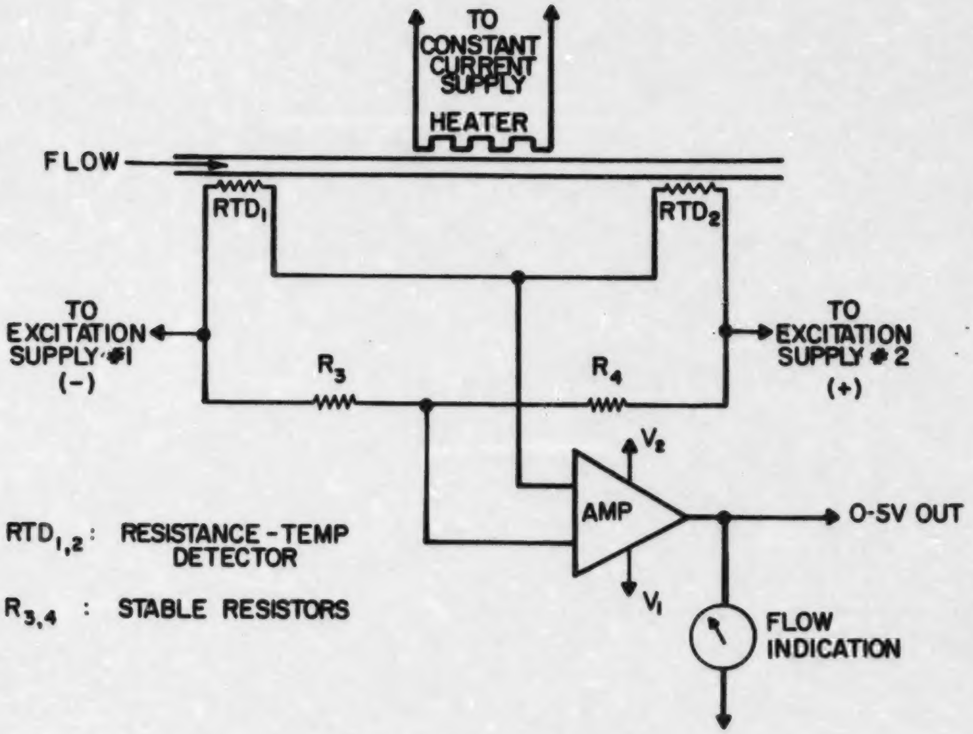
TO CONSTANT CURRENT SUPPLY
HEATER
FLOW
RTD$_1$
RTD$_2$
TO EXCITATION SUPPLY #1 (-)
TO EXCITATION SUPPLY #2 (+)
R$_3$
R$_4$
V$_2$
AMP
V$_1$
0-5V OUT
FLOW INDICATION
RTD$_{1,2}$: RESISTANCE-TEMP DETECTOR
R$_{3,4}$: STABLE RESISTORS

Figure 21. Schematic of Mass Flow Transducer.

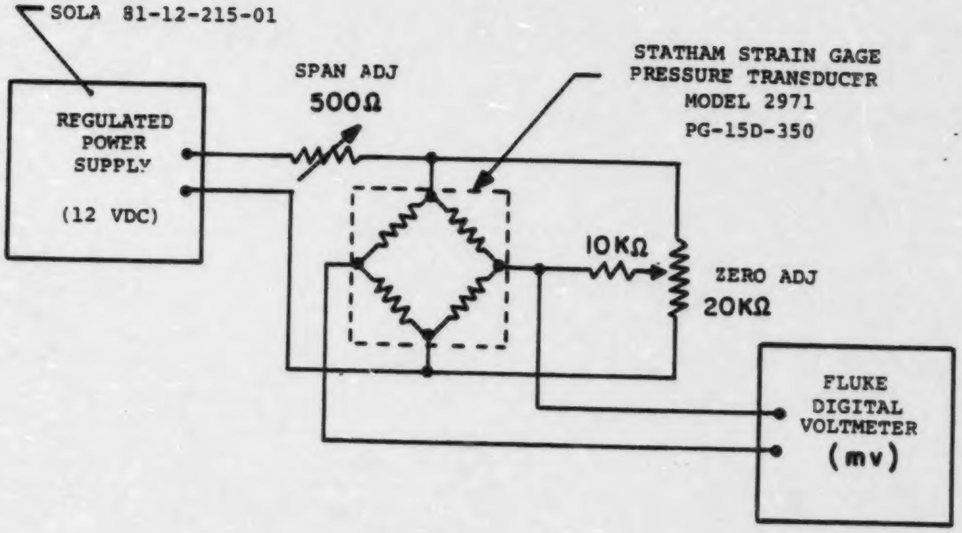
SOLA 81-12-215-01
REGULATED POWER SUPPLY
(12 VDC)
SPAN ADJ
500Ω
STATHAM STRAIN GAGE
PRESSURE TRANSDUCER
MODEL 2971
PG-15D-350
10KΩ
ZERO ADJ
20KΩ
FLUKE DIGITAL VOLTMETER
(mv)

Figure 22. Schematic of Differential Pressure Transducer.

There are several advantages to housing these instrumentation modules in one compact console. First, it is particularly advantageous in conducting detailed experiments with the TDU-GC to have at one location the controls and readouts of the various test parameters. In addition, by employing the versatile modular concept for the TDU instrumentation, future modifications to the TDU-GC can be readily accommodated.

SECTION 7

CHROMATOGRAPHIC SEPARATION AND ANALYSIS

Laboratory-scale thermal decomposition experiments rely strongly on the analysis of the chemical compounds that emerge from the high-temperature reactor. This analysis establishes the extent of thermal decomposition of the parent substance and at the same time provides information relative to the formation of thermal reaction products and products of incomplete combustion (PICs).

The seven stages of a typical instrumental chemical analysis are as follows:

1. Collection
2. Storage
3. Extraction
4. Concentration
5. Isolation
6. Identification
7. Quantification

The primary function of the GC located in the TDU-GC assembly is to separate the constituents of the various complicated chemical mixtures. In addition, this GC unit is also responsible for stages 4 and 7 of the above analysis scheme.

Another vital function of the TDU-GC separation column is to trap the condensable products that emerge from the high-temperature reactor. A chromatographic column can indeed be an excellent trap, and if held at cryogenic temperatures, it can quantitatively capture most substances having a molecular weight of~50 or greater. This thermal focusing process (5) is a crucial step in the sample handling with the TDU-GC. Also, for the analysis of products from the TDU-GC, programmed temperature GC is essential.

The gas chromatograph that is incorporated into the TDU-GC system is a basic Varian 3700 instrument. This GC instrument is capable of high-resolution gas chromatographic performance, and also it is capable of cryogenic programmed temperature GC operation. Numerous different detectors can be used with this instrument. For example, the electron capture detector, the hydrogen flame ionization detector, the flame photometric detector, ultraviolet detectors, and thermionic specific detectors can be employed with this particular gas chromatograph. It can also be adapted to accept the Hall electrolytic conductivity detector. Data handling with the Varian instrument is accomplished with a CDS-111 dedicated microprocessor or the CDS-401 data handling terminal.

The TDAS depends on high-resolution separation of the various chemical compounds. Therefore, this necessitates the use of capillary GC columns. The columns that are presently used in the TDU-GC are 0.25 mm ID OTC's that have 0.25 micron thick silicone phases. The columns that are usually used in the TDU-GC are from 10 to 20 meters long. However, the columns that are used in the other GC's which support the TDU-GC operation, are much longer; consequently, higher efficiency separations can be obtained with these instruments. Presently, the separation capability within the TDU-GC is adequate for the samples currently being tested. In the future, other types of OTCs will also be incorporated in the TDU-GCs. These will contain chemically bonded stationary phases (23) and other types of high-temperature substrates.

The gas flow to and from a gas chromatograph must be especially free of extraneous organic contaminants. Otherwise the chromatographic separation and subsequent analysis are adversely influenced by these contaminants (24). Also, the geometry of the flowpath should be free of mixing regions and unswept recesses (25). In a system as complicated as the TDU-GC, there are a number of potential sources for organic contamination. However, by using thermally stable materials throughout the gas flowpath, the level of bleed contaminants can be minimized.

SECTION 8

PREPARATION OF SAMPLES FOR TDU-GC TESTING

Conducting experiments with the TDU-GC requires considerable attention on the part of the analyst that is operating the various components of the system. To conduct appropriate experiments, it is necessary that sample preparation be carefully conducted and that each step of the experiment procedure be conducted in proper sequence.

Test samples that are to be introduced into the TDU-GC can be prepared in their final form within the confines of the glove box that surrounds the entrance to the sample insertion region of the TDU-GC. Prior preparation of toxic organic substances should be conducted in a preparative laboratory that has the appropriate safety features. Once the sample that is to be tested has been prepared, it can be placed within the glove box by removing one of the rubber gloves from the front end of the chamber. During the placement of the sample in the glove box, it is also necessary to include the additional sample handling materials, that is, syringes, probes, tissues, activated charcoal, containers for disposal of tissues and waste solvents, additional sample vials, and other sample handling components. After all of the necessary pieces of equipment are located within the glove box, the rubber gloves can then be firmly attached, and a small flow of nitrogen gas can be admitted to the glove box interior. A fresh charcoal trap should likewise be installed at the exit location of the glove box.

Sample handling procedures have been developed for gaseous samples, highly volatile liquid samples, low volatility liquid samples, and also solid organic samples. The gaseous organic samples are generally highly diluted in a gas sampling container (5) and, then introduced with a gas-tight microliter syringe into the sample insertion region of the TDU-GC. Volatile organic samples can also be diluted and handled as a gas-phase sample, or they can be injected with a suitable liquid syringe. The difference between these two techniques basically depends upon the volatility of the organic species.

For low volatility organic samples, a microliter syringe can be used for sample introduction, however, in most cases the sample of interest will have to be diluted with a suitable solvent. Solid organic samples can be handled using either a sample probe injection technique, or they can be dissolved in a suitable solvent and injected with a syringe. In most cases, it is desirable to evaporate the solvent prior to initiating the thermal decomposition test. Complex industrial organic waste samples can be handled either with a syringe injection technique or with the use of one of various sample insertion probes.

Once a sample has been inserted into the TDU-GC, it is necessary to dispose of the various sample handling materials (i.e., the tissues and spent solvents) in a safe manner. A capped plastic jar containing charcoal can be used for the temporary containment of the used laboratory tissues. A waste solvent container can be temporarily used for holding the used solvents.

After a series of tests has been completed with a given sample and the glove box interior has been adequately swept with purge gas, one of the gloves can be removed from the front of the glove box. The spent and waste materials can then be removed for appropriate permanent disposal.

SECTION 9

DETAILED INSTRUCTIONS FOR OPERATING A TDU-GC SYSTEM

The conducting of thermal decomposition tests with the TDU-GC system requires considerable attention to detail. If any of the steps in the experimental procedure are conducted out of sequence, satisfactory data will not be obtained. In fact, if some steps are not performed in their proper sequence, certain components of the TDU-GC system could be damaged.

INITIAL SYSTEM PREPARATION PROCEDURES

Step a: To prepare the TDU-GC system for operation, it is first necessary to establish an inert gas flow through the entire TDU-GC system. Eventually, all of the components will be cleansed using a flow of gas at extremely high temperatures. During this initial preparation of the system it is also necessary to open the valve on the cryogenic coolant tank (liquid nitrogen with a 50 to 80 psig delivery pressure).

Step b: The heat transfer line between the high temperature thermal reactor and the gas chromatograph, along with the column inlet region, must be heated, and this is accomplished by activating the West controller and the auxiliary thermal control of the gas chromatograph. Normally during initial conditioning, and thereafter, this transfer line is heated to approximately 250°C.

Step c: The sample insertion region is next heated to an elevated temperature, and this is accomplished by activating the Theall Engineering temperature controller. The photograph presented in Figure 23 shows the method for manually setting the thumb wheel dial to the desired temperature for the sample insertion region. A sample insertion temperature of approximately 275°C should be obtained for the initial daily preparation of the system.

Step d: A small flow of heat transfer air should next be established at both the front end and at the rear cavity of the thermal reactor quartzware. This is accomplished by use of the two transfer air flow control valves located on the gas flow control module. (These adjustments will be discussed later in the "Standard TDU-GC Experimental Procedure.")

Step e: Power is then applied to the Lindberg furnace and all three heating zones are adjusted to a temperature of approximately 300°C. This temperature has been found to be adequate for both cleansing the reactor flowpath and, in most cases, it is also a satisfactory temperature for the initial quantitative transport of admitted samples.

Step f: With a flow of inert gas established, it is then necessary to attach the second of the two flow restrictors, that is, the 80 cm by 0.25 mm ID stainless steel restrictor. Figure 24 shows the attachment of this stainless steel flow restrictor to the exit tube. (The attachment of this restrictor is necessary to pressurize the gas flow in the gas chromatograph.) After the flow restrictor has been connected with silicon rubber tubing, it is then necessary to increase the gas flow through the system, and this is accomplished by adjusting the precision Porter gas flow control valve located on the gas flow control module. For system cleansing purposes, an inlet pressure of approximately 1.5

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Figure 23. Activation of the TECO Temperature Controller.

Figure 24. Attaching the Stainless Steel Flow Restrictor.

absolute atmospheres is generally sufficient for the daily preparation of the system (the adjustment of the precision Porter gas control valve will be discussed later on in this section).

Step g: After establishing that there is an acceptable gas flow throughout the system (this can be verified by a simple flow measurement at the restrictor exit shown in Figure 24), the gas chromatograph can be subjected to a programmed temperature sequence, e.g., 10°C per minute. Normally the maximum temperature of the program is approximately 10°C higher than the final temperature at which the analytical chromatographc data would be obtained, e.g., 250 to 275°C. During this thermal conditioning and cleansing of the system, as well as the gas chromatograph, the chromatographic output signal can be monitored providing the detection and amplification portions of the chromatographic system have also been activated.

Step h: After allowing the gas chromatographic oven and its column to experience the elevated conditioning temperature for approximately 20 minutes, the temperature control of the sample insertion chamber can be reduced to ambient temperature in anticipation of the initial insertion of sample. Usually the first determination is a quantitative transport of the particular test sample through the TDU-GC system, and this is conducted at temperatures and test conditions that would be non-destructive to the organic gas-phase sample.

Step i: The gas chromatographic column assembly can then be returned to the initial subambient starting temperature, and this is accomplished automatically with the Varian gas chromatographs.

Step j: During the conditioning, the column and the heating of the different transport regions of the TDU-GC, the GC inlet region, would also have been maintained at an elevated temperature. Consequently, prior to conducting a test with the TDU-GC system, it is necessary to return this heated GC inlet region to a 0°C setting using the auxiliary thermal control on the gas chromatograph.

Step k: As the cryogenic cooling system had been activated earlier, the gas chromatographic column oven interior will eventually reach subambient temperatures and hold at this preselected low temperature. After the column oven interior has reached this low temperature, the large splitter restrictor can be removed (see Figure 24). Prior to conducting the first test with the cleansed TDU-GC system, it is necessary for the sample insertion chamber also to reach a temperature that approaches ambient. After the sample insertion chamber has reached a temperature in the vicinity of 30° to 45°C, the TDU-GC system is ready for conducting a thermal decomposition experiment. This completes the initial preparation of the TDU-GC system.

STANDARD TDU-GC EXPERIMENTAL PROCEDURE

Step A: With the TDU portion of the system and the gas chromatograph at their initial conditions, i.e., an inert gas flowing in the system, the large flow restrictor removed, a cool sample insertion region, and the GC column at a subambient temperature, the system is then ready for the admitting of a test sample.

Step B: After selecting the experimental test conditions, it is necessary to establish these conditions within the TDU-GC system. Accordingly, the test temperature is selected by adjusting each of the three zones of the Lindberg furnace as shown in Figure 25. All three zones are maintained at the same approximate temperature. To converge on the exact temperature for the reactor, it is necessary to make final stepwise adjustments on the center zone of the Lindburgh furnace and the precise readout that corresponds to the reactor temperature is the Omega digital thermometer that is located on the temperature control module of the instrumentation console. Normally, the final reactor temperature is adjusted to within ±1°C.

Step C: A rough calculation for the gas flow through the TDU is then made, and this calculation uses equation (7) that is presented in Section 6 of this report. The voltage that corresponds to the calculated flow value would accordingly be read out on the digital VOM which monitors the output from the mass flow transducer. The gas flow adjustment is made by rotating the ten-turn Porter precision flow control valve as shown in Figure 26. Initially, only a first approximation of the final flow is selected using this flow control device.

Step D: The next procedure that must be carried out is the switching to the test gas, that is, the flowing atmosphere under which the thermal decomposition test is to be conducted. If the test is being conducted in air, then a gas cylinder of breathing quality compressed air will be installed and this gas stream will be connected to channel B of the gas flow control module. If other oxygen containing gas mixtures are used, then a special high pressure tank containing this mixture would be connected to the B channel of the flow control module. If the test atmosphere were nitrogen, or some other inert gas (helium, argon, etc.), then these compressed

Figure 25. Adjustment of the Lindberg Furnace Temperature;

Figure 26. Gas Flow Adjust using the Porter Precise Flow Control Valve.

gas cylinders would be attached to the A channel of the gas flow system. Therefore, depending upon whether a high-temperature oxidation test was conducted or an inert gas was to be flowing through the reactor, this particular gas stream would now be selected using the gas switching valve shown in Figure 27. This is a two position rotary valve, and it is important that the valve be rotated to the appropriate gas stream. (Caution: it is of utmost importance that an oxygen containing carrier not be admitted to the gas chromatograph when the column would be experiencing elevated temperatures.)

Step E: After taking the various measurements of the test's parameters as expressed in Equation (7), it is necessary to measure the barometric pressure, the ambient temperature in the vicinity of the flow and pressure transducers, and a measurement is required of the reactor internal pressure, i.e., the pressure corresponding to this earlier adjusted flow value. After these measurements have been made, it is then possible to make a refined calculation of the required flow corresponding to a given residence time at the established reactor temperature. The voltage corresponding to this mass flow can then be dialed off as previously shown in Figure 26.

Step F: To establish an appropriate square-wave temperature versus time profile for migrating gas-phase molecules, it is necessary to adjust the heat-transfer air flows that control temperature both upstream and downstream of the race-track configuration quartz reactor. This is accomplished by adjusting carefully the two valves that control both streams of heat transfer air. Figure 28 is a photograph showing the adjustment of these two airstreams.

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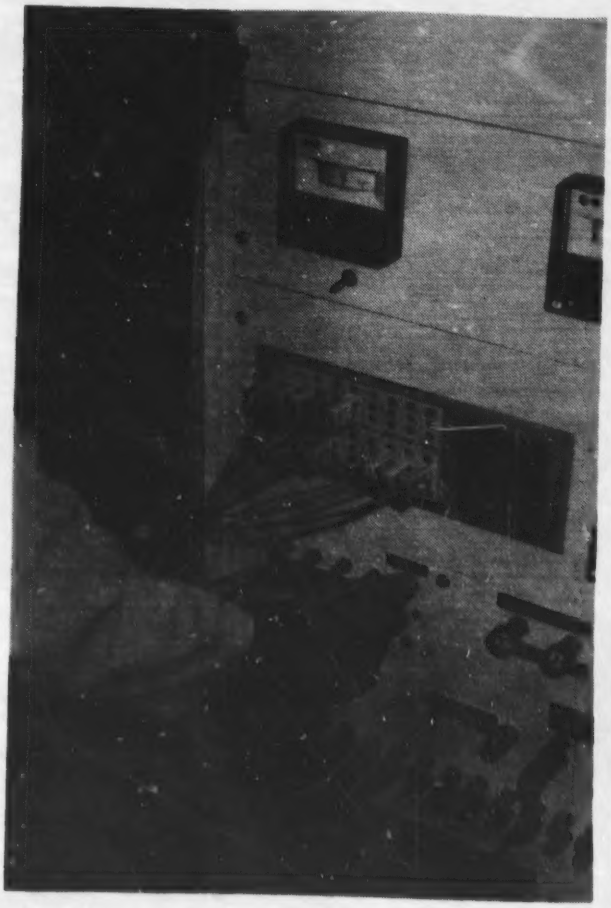

Figure 27. Switching to the Inert Gas Stream.

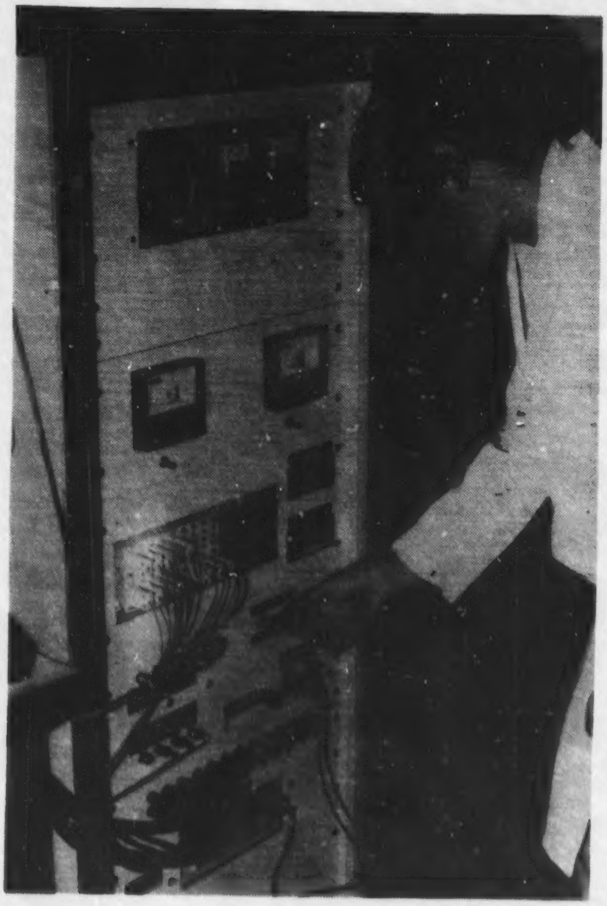

Figure 28. Adjusting the Heat Transfer Air Flows.

Step G: The TDU-GC system is now close to being ready for accepting a sample; however, just before making a sample insertion it is necessary to again monitor the various system temperatures and to determine that they fall within acceptable limits. The temperature-selector switch on the temperature measurement module is then rotated (see Figure 29) to display the various component temperatures which are indicated by the selector switch thermocouple thermometer. If any of these measured temperatures are not within their acceptable limits, then appropriate corrections should be made so that they are within limits prior to injecting the test sample. Also, just prior to injecting the sample, it would be desirable to again monitor the internal reactor pressure and the voltage corresponding to the mass flow through the TDU.

Step H: A sample probe or syringe (either for liquids or gases) is then cleaned and prepared for handling a sample. A probe would have previously been cleaned in a suitable solvent and allowed to dry prior to admitting a sample. A gas-tight syringe would normally be filled and exhausted several times with the test gas sample. Normally, the gas-tight syringe would be cleaned with a special vacuum line between fillings with different organic gas-phase samples. A liquid syringe would be likewise thoroughly cleaned between different samples.

Step I: With a loaded sample probe, it is a matter of removing the sealed insert from the sample insertion region and inserting the loaded probe into the interior of the sample insertion chamber. When using a syringe for injecting sample, the syringe would be loaded using a procedure whereby a larger than the intended delivery quantity would be drawn into the syringe. The excess would

Figure 29. Monitoring the Various TDU Temperatures.

Figure 30. Inserting a Sample from the Glove Box.

then be exhausted into the vial or container prior to inserting the syringe through the silicon septum at the entrance to the sample insertion chamber. Before sample insertion, the syringe needle would be wiped once with a disposable lintless tissue which would be immediately deposited in a special screw-top jar that is partially filled with granulated charcoal. After inserting the syringe needle to full depth of the injector assembly, the syringe plunger would be steadily depressed and the syringe would be quickly retracted from the sample insertion chamber (see Figure 30).

Step J: The sample insertion chamber would next be subjected to a pre-selected programmed increase in temperature using the TECO temperature programmer. Specifically, power would be turned on to the temperature programmer, and the programming rate would be established. Usually, temperature programming rates from 10° to 25°C per minute are used for heating the sample insertion region to temperatures in the vicinity of 300°C (see the earlier Figure 23). At the same time that the temperature programmer is activated, a clock is started and a fixed period of time (usually 15 minutes) is alloted for transporting of the gas-phase sample into and through the high-temperature reactor.

Step K: After the sample insertion chamber has been heated for this fixed period of time, the TDU system is switched to an inert gas flow (if necessary) in the manner as indicated in Figure 31, and a five minute period is set aside for the inert gas to sweep all regions of the TDU-GC including the gas chromatographic column. At the same time, the TECO temperature programmer is turned off and the sample insertion region is allowed to gradually return to ambient temperature.

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Figure 31. Switching to Test Gas Stream.

Figure 32. Activating of the Terminal Data System.

Step L: After adequately sweeping the gas flowpaths with an inert carrier gas, the column inlet region between the reactor and the gas chromatograph is heated to a transport temperature, usually approximately 250°C. After this sample entry region has obtained thermal equilibrium (a process that requires almost four minutes), the data system of the gas chromatograph is prepared for taking data. This is accomplished with the Varian 401 system by pressing the "data sys" key (see Figure 32), and in about fifteen seconds the lower "ready" light on the instrument will indicate that the system is ready for accepting raw chromatographic data.

Step M: Next it is necessary to pressurize the gas chromatographic column. This is accomplished by installing the large splitter restrictor (80 cm long by 0.25 mm ID). Also, at the same time an inlet pressure is established by adjusting the gas flow control valve on the TDU-GC console to a value that would produce an optimum gas flow through the GC column. This value will depend upon the dimensions of the open tubular column, but usually a 5.0 psig head pressure is quite adequate for a 15 meter by 0.25 mm capillary column.

Step N: After the inlet pressure has equilibrated as evidenced by the inlet pressure transducer, the gas chromatographic sequence can be initiated by depressing the injection switch as shown in Figure 33.

Step O: The output chromatographic data, i.e., the chromatogram, will then be recorded either on the strip chart recorder or on the Varian Vista 401 data terminal. To obtain appropriately displayed chromatographic peaks it may be necessary to change the attenuation throughout the recording of the chromatograph. Consequently,

Figure 33. Starting the Gas Chromatographic Sequence by Depressing the Injection Switch.

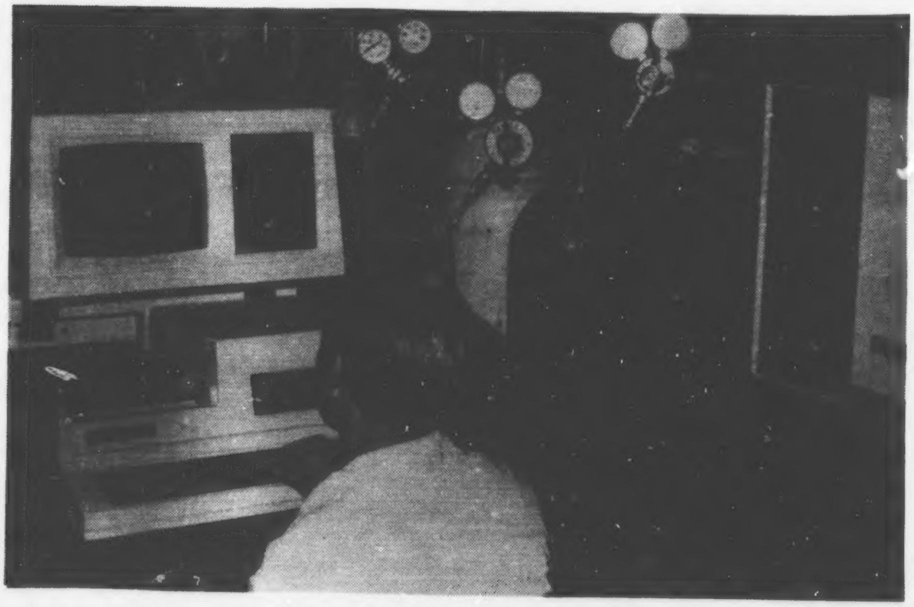


Figure 34. Monitoring the Chromatogram Generation.

periodic monitoring of the chromatogram generation is sometimes advisable (see Figure 34). At the completion of the programmed temperature GC separation, the numerical data are rapidly processed by the chromatographic data handling equipment.

Step P: This completes the sequence for one thermal decomposition test using the TDU-GC system. Prior to performing the next experiment with the system, it is necessary to cool the column inlet region of the gas chromatograph to a temperature that approaches ambient and after the gas chromatographic oven interior has returned to its initial sub-ambient temperature, the large flow restrictor can be removed in preparation for the next thermal decomposition experiment.

SECTION 10

EXAMPLES OF THERMAL DECOMPOSITION STUDIES USING THE TDU-GC SYSTEM

Precise thermal decomposition experiments can be conducted using a TDU-GC. This laboratory system is capable of investigating a wide variety of organic materials and experimentally examining the effects of various thermal decomposition variables. This system can rapidly handle pure organic compounds and also very complex industrial organic waste mixtures.

A TDU-GC system can be used to: a) establish the thermal decomposition profile of a substance, b) determine the residence time effects and associated kinetic behavior, c) investigate different gaseous atmospheres, pressure effects, and other related thermal decomposition variables, d) collect data for prediction of thermal decomposition behavior, and e) provide guidance for larger scale thermal disposal operations.

To demonstrate the versatility and broad application of the TDU-GC, examples from three separate studies (17,18,26) which utilized the TDU-GC are presented.

Assessing the Thermal Decomposition Behavior of Selected Polynuclear Aromatic Hydrocarbons

Although numerous chlorinated hydrocarbons have been studied with respect to their thermal decomposition behavior, very little is known about the thermal decomposition behavior of polynuclear aromatic hydrocarbons (PAHs). Consequently, a study was initiated where several selected PAHs were subjected to thermal decomposition tests using the TDU-GC. Many PAH compounds demonstrate carcinogenic activity, consequently, data pertaining to their permanent disposal by high-temperature incineration is of interest.

In this study (18) several chlorinated naphthalenes and PAHs were subjected to a series of thermal decomposition analyses. Specifically, benzo-e-pyrene, monochloronaphthalene, 1,2-dichloronaphthalene, 1,2,3,4-tetrachloronaphthalene, anthracene, triphenylene, and benzene were dissolved in reagent grade cyclohexane (0.2% w/w sample in solvent) and subjected to thermal exposures in flowing air at elevated temperatures. A chromatogram of the aromatic mixture is shown in Figure 35. After dissolving this sample in solvent, it was inserted into the TDU-GC with the use of a syringe. These tests were conducted with a mean residence time exposure of 2.0 seconds. The composited sample was subjected to thermal exposures ranging from 400°C to 725°C in flowing air, and the resultant thermal decomposition profiles for these compounds are presented in Figures 36 and 37.

From the above data, it is evident that the PAHs studied in this investigation possess considerable thermal stability in air. These data also show triphenylene, benzo-e-pyrene, and anthracene exhibiting markedly greater decomposition at the higher temperatures when compared with naphthalene and the chlorinated naphthalenes. (The triphenylene profile in Figure 37 represents an average of the non-chlorinated PAH behaviors as depicted in Figure 36.)

The chlorinated naphthalenes exhibited thermal stabilities in this investigation very similar to those observed in previous

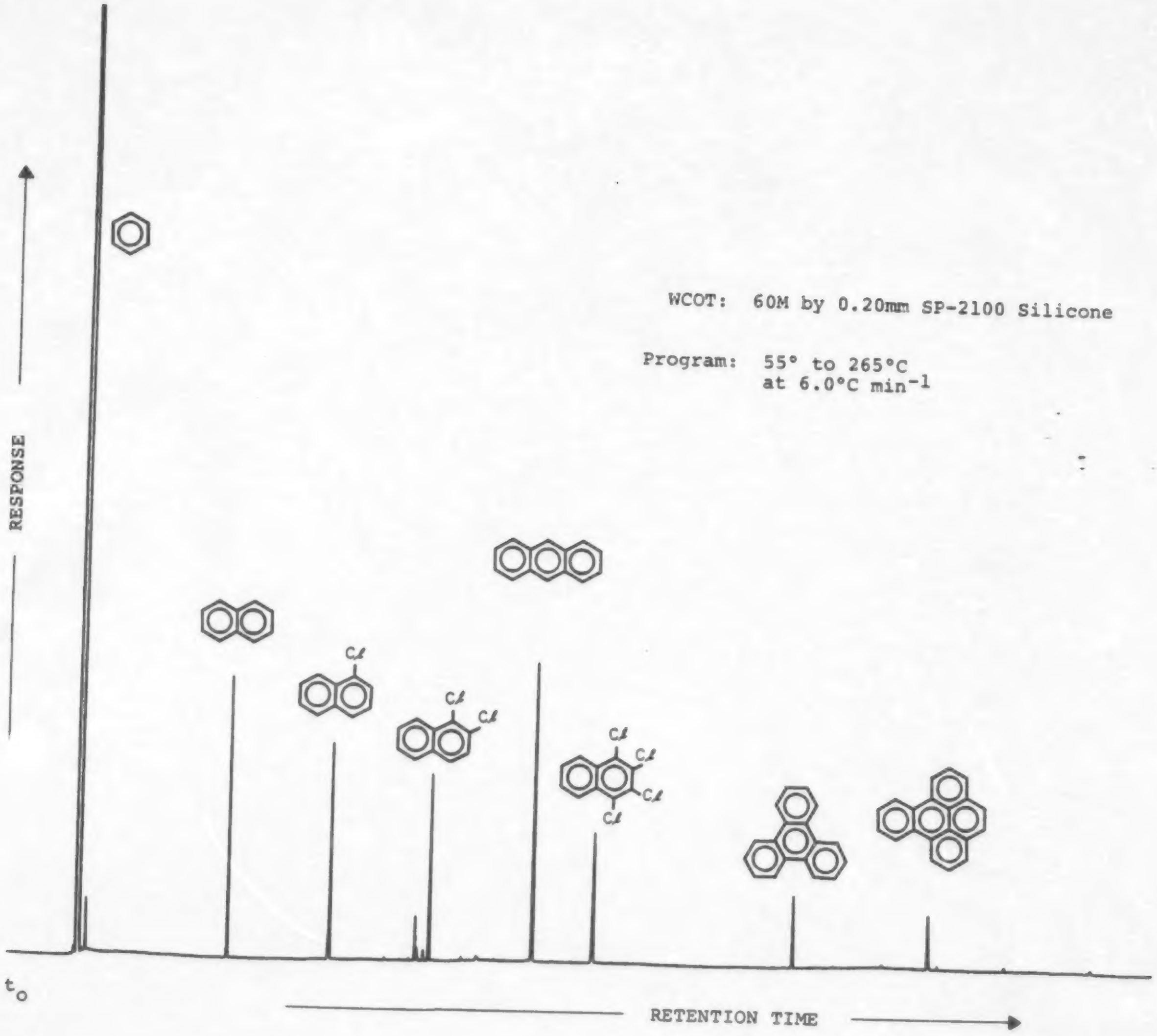


Figure 35. Chromatogram of PAH Compounds.

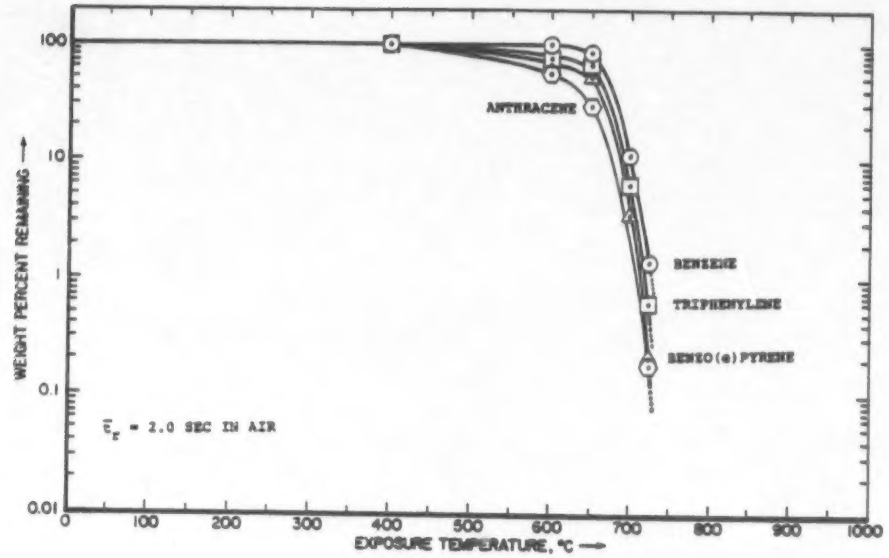


Figure 36. Thermal Decomposition Curves for Benzene, Triphenylene, Benzo[e]pyrene, and Anthracene.

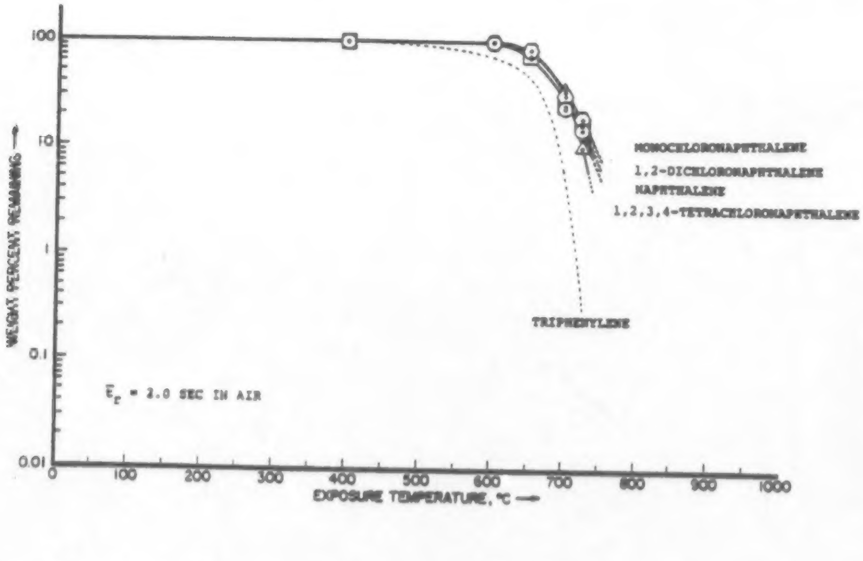


Figure 37. Thermal Decomposition Curves for Monochloronapthalene, 1,2-Dichloronaphthalene, Naphthalene, and 1,2,3,4-Tetrachloronaphthalene.

studies (4) of chlorinated biphenyls, brominated biphenyls, chlorinated dioxins, chlorinated furans, and various chlorinated benzenes.

In addition, the higher molecular weight non-chlorinated PAHs (i.e., anthracene, triphenylene, benzo-e-pyrene) exhibit lower thermal stabilities than those associated with some halogenated aromatic compounds.

Additional studies are needed to establish whether PAHs as a general class display similar thermal decomposition behaviors. Also, determining the effects of other thermal decomposition variables (e.g., degradation in an oxygen starved atmosphere) would provide valuable insight into the processes involved in the high-temperature gas-phase thermal decomposition of PAHs.

The Effect of Gas-Phase Residence Time Upon the Thermal Decomposition of Chlorinated Benzenes

Chlorinated benzenes have been found to demonstrate considerable thermal stability. In addition, there is wide spread interest with respect to the environmental impact of various chlorinated benzenes.

In a recently completed study of the thermal decomposition behavior of chlorinated benzenes (26) it was observed that the gas-phase residence time had a highly predictable effect upon the extent of thermal decomposition. Figures 38 through 41 show in a sequential manner the effect of different gas-phase residence times upon the thermal decomposition of four selected

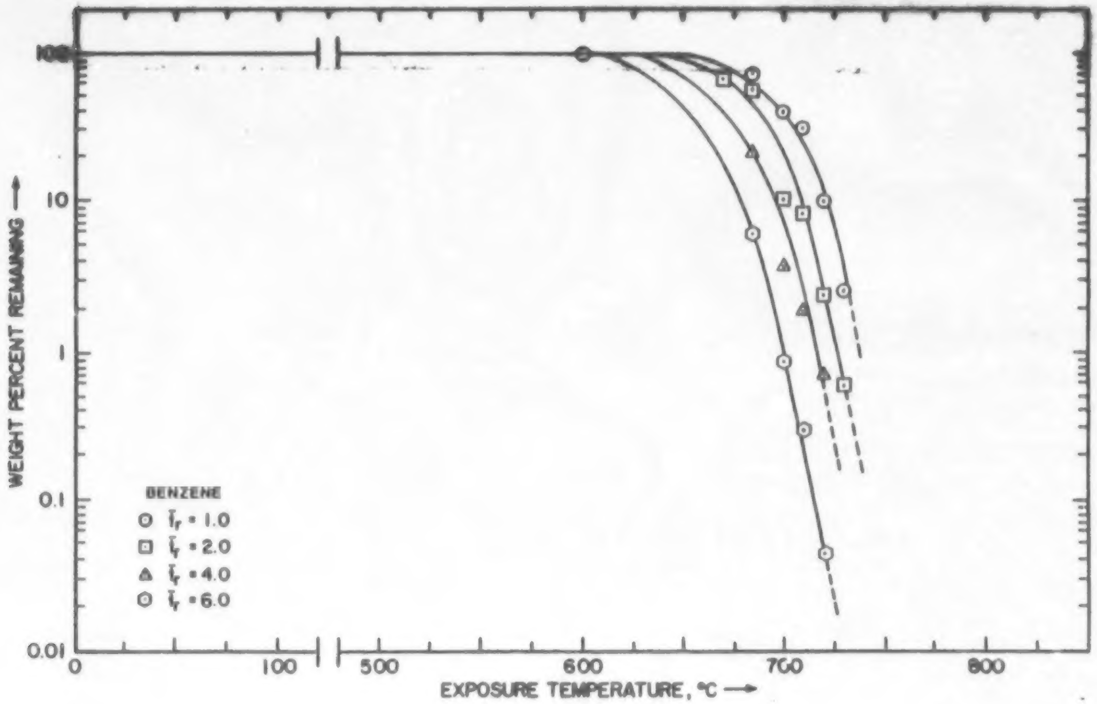


Figure 38. Thermal Decomposition of Benzene at Different Residence Times.

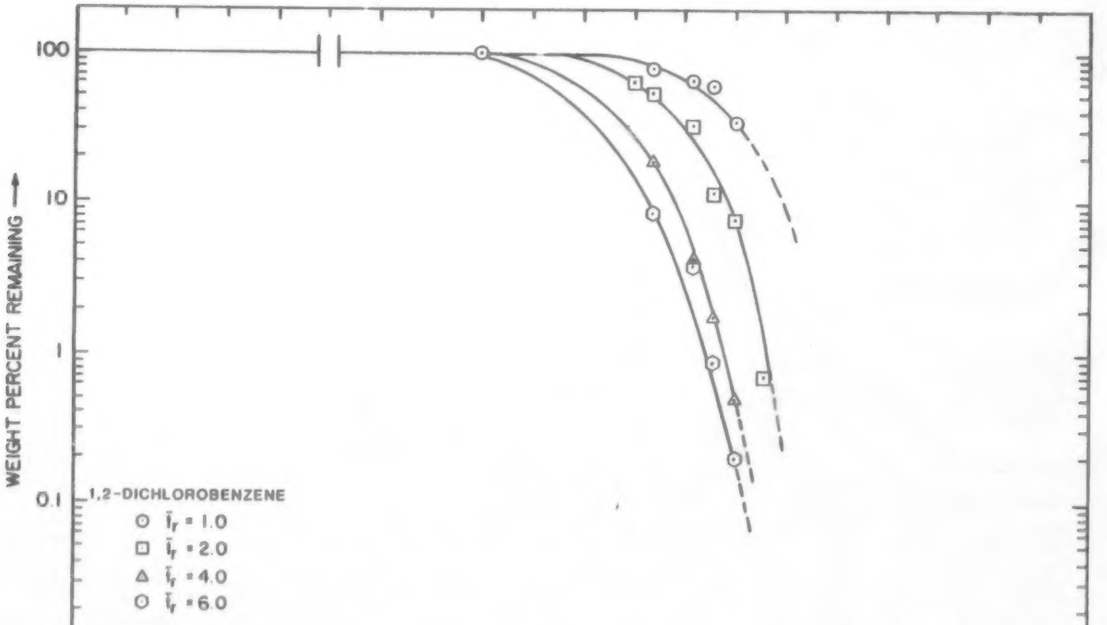


Figure 39. Thermal Decomposition of 1,2-Dichlorobenzene at Different Residence Times.

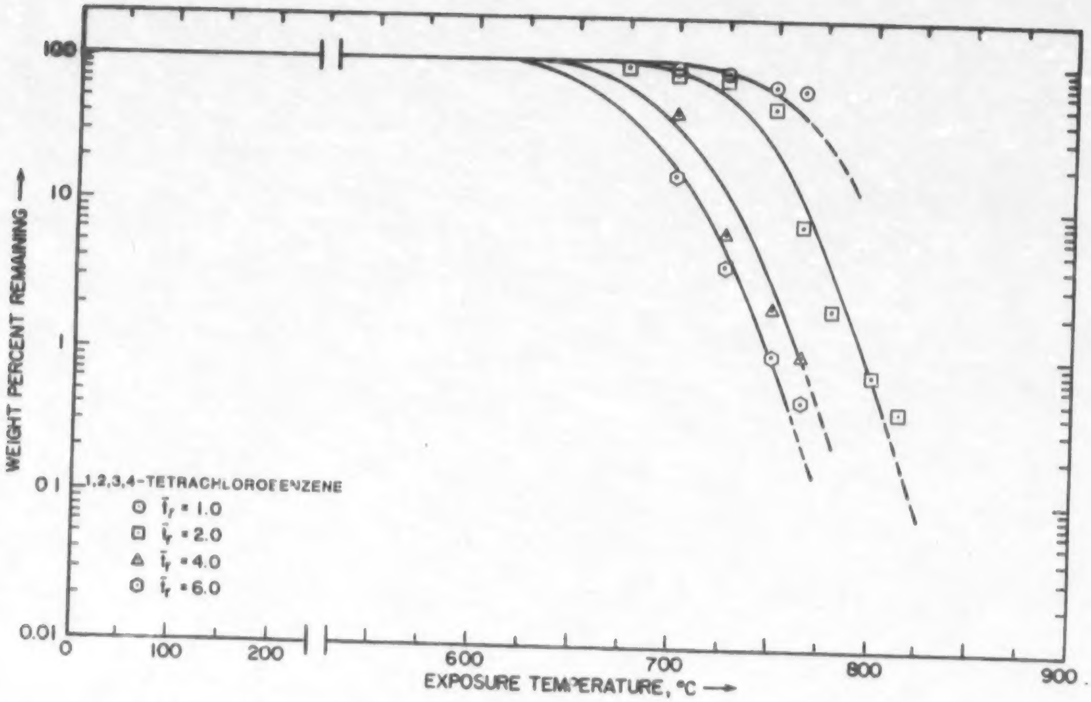


Figure 40. Thermal Decomposition of 1,2,3,4-Tetrachlorobenzene at Different Residence Times.

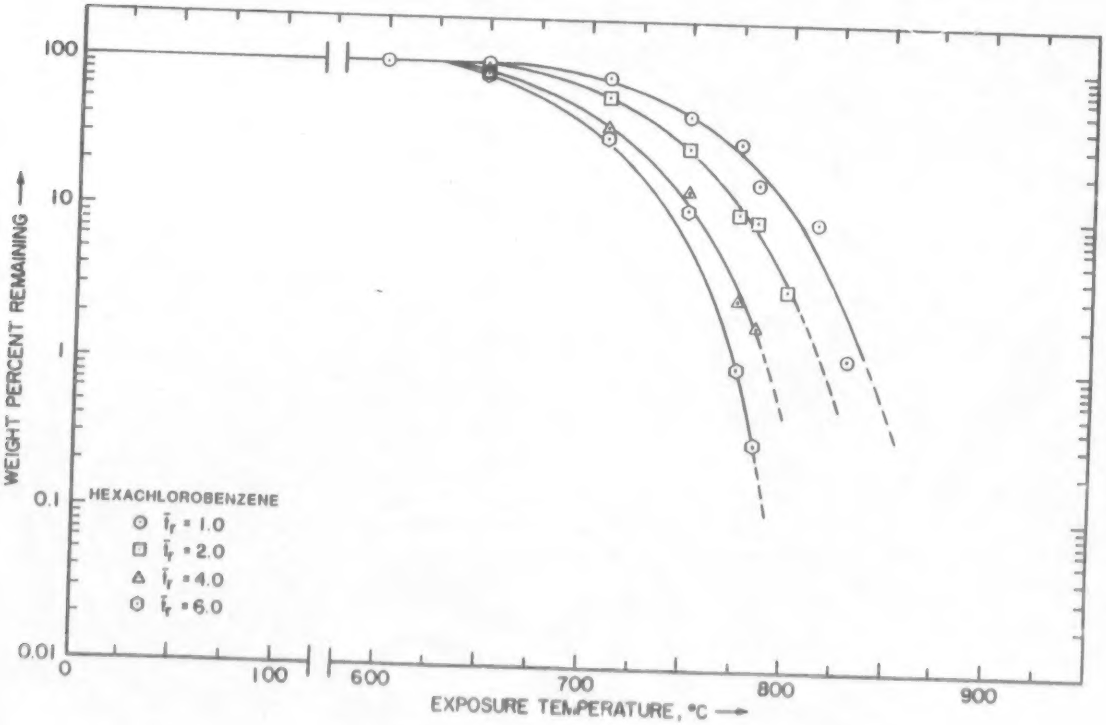


Figure 41. Thermal Decomposition of Hexachlorobenzene at Different Residence Times.

aromatic compounds in flowing air. The data presented in this example is a small portion of the information resulting from the study (26) of chlorinated benzenes. However, notice in each case the orderly affect of different mean residence times upon the thermal decomposition of the gas-phase species.

Once again, it was shown in this study that hexachlorobenzene is an especially thermally stable substance. In practically every previous case where chlorinated hydrocarbons were subjected to thermal decomposition experiments, we have found hexachlorobenzene as a stable product of incomplete combustion. In fact, of the various chlorinated benzene compounds studied thus far, hexachlorobenzene has demonstrated the greatest thermal stability.

Complex Industrial Organic Waste Mixture

To further demonstrate the versatility of the TDU-GC, an extremely complex blended waste sample (17) was prepared and examined using the TDU-GC system. This particular composited sample consisted of several waste streams which individually were: a chlorinated still-bottom sample, a processed creosote waste, a hydrocarbon sample that originated from oil shale, a pyrolyzed nitrile polymer waste, a waste containing mixed DDTs, and small quantities of chlorinated aromatic hydrocarbons (e.g., chlorinated benzenes, naphthalenes, and biphenyls).

Figure 42 shows a HRGC chromatogram of this composited industrial waste sample, and indeed it would be difficult to imagine a more complicated mixture of organic compounds. (Notice that this chromatogram is in two sections). This particular HRGC

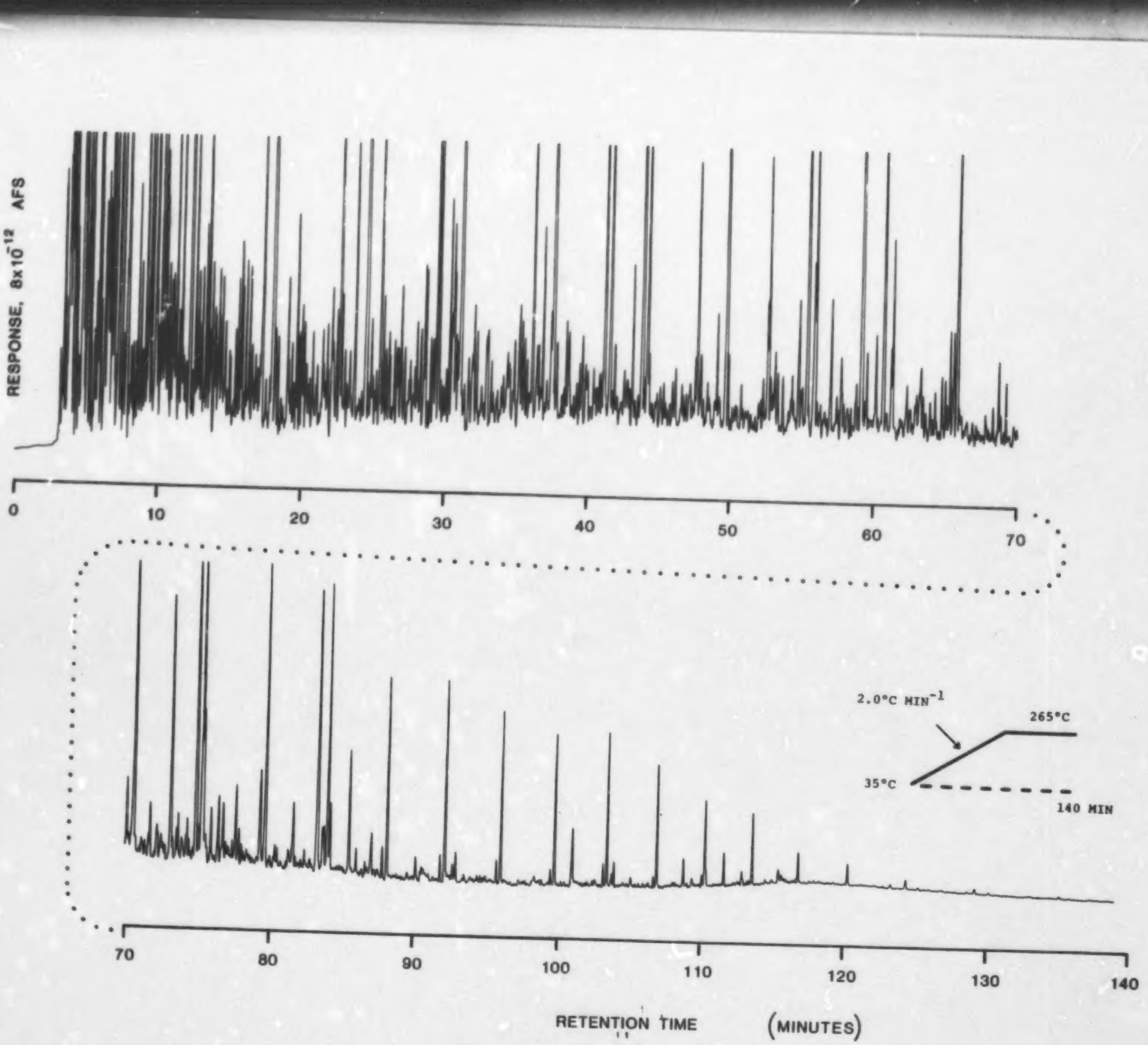
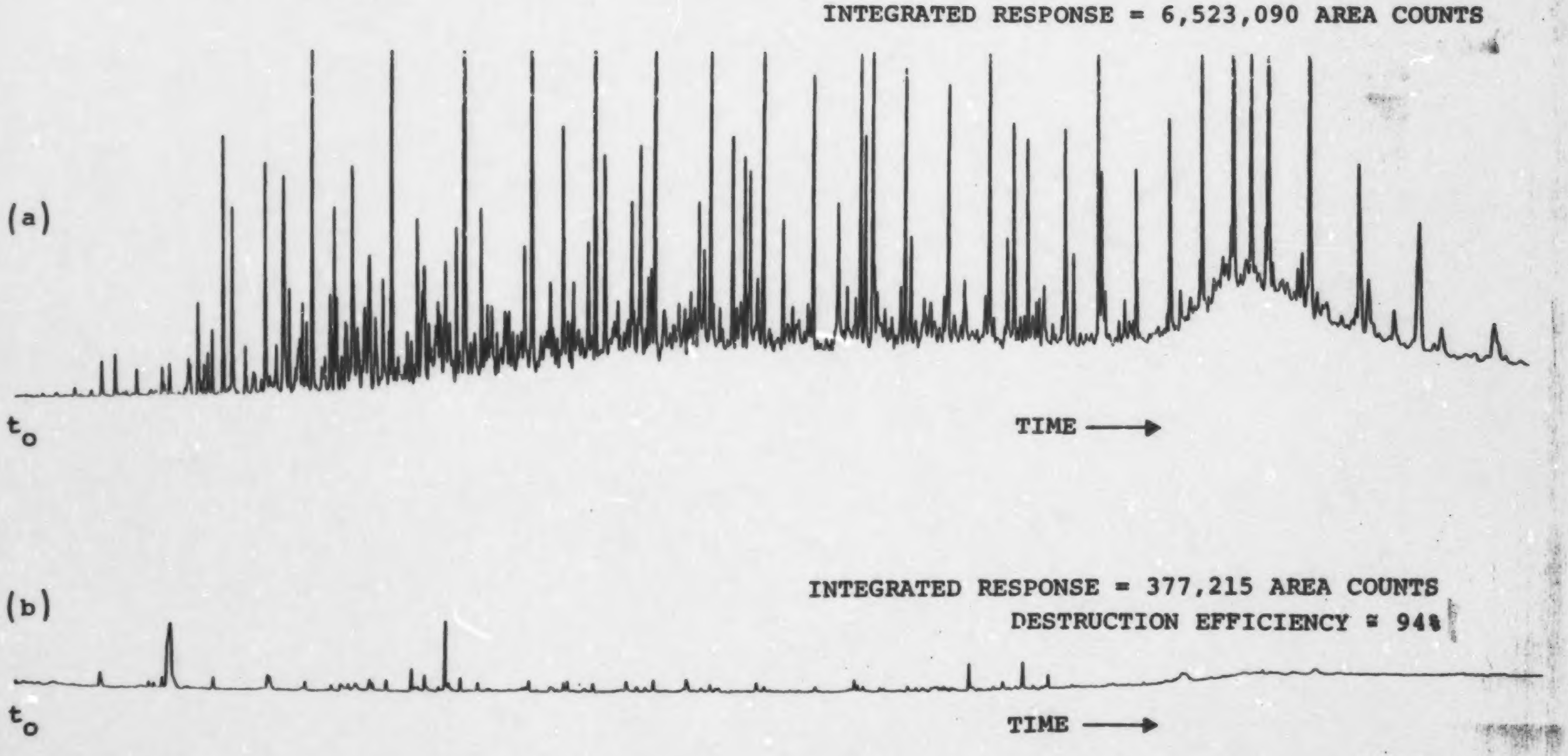


Figure 42. HRGC Chromatogram of Composited Waste Sample.

chromatogram was obtained using a special modified GC instrument that is dedicated to developing analytical techniques for highly complex organic samples. The chromatographic tracing shown in Figure 43a represents the same composited sample only in this case it was subjected to a 300°C exposure in flowing nitrogen using the TDU-GC system. Also, this analysis was performed with a relatively short open tubular GC column. Figure 43b presents a chromatogram of the same sample after it had been exposed to a 690°C thermal exposure in flowing air for a mean residence time of 2.0 seconds. It is interesting to note how simple the 690°C effluent sample has become, as many of the fragile organic constituents have been thermally decomposed to complete decomposition products, e.g., H_2O, CO_2, HCl, etc.

Some very important thermal decomposition information is contained in the chromatogram of Figure 43b. Therefore, to clearly show this information, the chromatogram has been reconstructed in skeletal form and presented in Figure 44. The skeletal chromatogram shows many thermally stable parent compounds. However, there are also other compounds present in this chromatogram that were not prominent in the earlier GC tracings. These compounds, which are identified and designated by the arrows in Figure 44, have been found in previous studies (1,4,13,16) to be products of incomplete combustion (PICs). In short, the chromatograms shown in Figures 43b and 44 correspond to those compounds (POHCs and PICs) that would seriously challenge an incinerator with respect to incinerability (27). Also, it is these compounds that would be of interest with respect to further toxicological study.



F ure 43. TDU-GC Chromatogram of Composited Waste Sample.

a) T = 300°C, $\bar{t}_r$ = 2.0 sec.
b) T = 690°C, $\bar{t}_r$ = 2.0 sec.

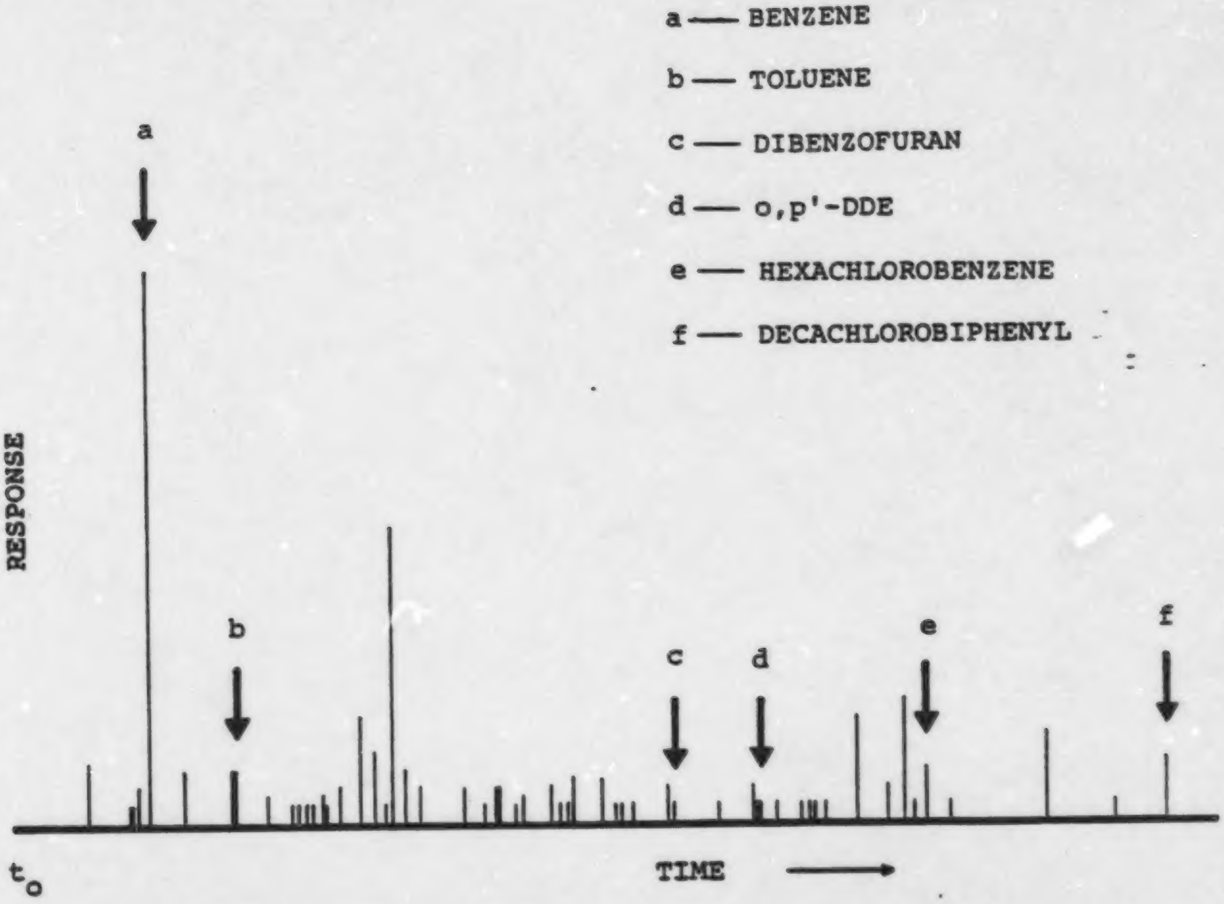


Figure 44. Skeletal TDU-GC Chromatogram of the Composited Waste Effluent.

SECTION 11

MAINTENANCE AND TROUBLESHOOTING A TDU-GC SYSTEM

Some parts of a TDU-GC system are relatively delicate. For example, the quartzware components near the sample insertion region and the quartz tubing at the outlet of the thermal reactor are rather fragile and any abuse, movement, or large displacement of components in these regions may very likely break the high-temperature quartz tubular reactor assembly. In view of the fragile nature of the quartzware, the TDU-GC should be assembled on a firm bench in a laboratory that has concrete floors. Also, this laboratory should have temperature, humidity, and dust control. Other parts of the TDU-GC system are relatively rugged or sturdy and by their design require a minimum of care and attention.

With respect to troubleshooting faulty components in a TDU-GC system, this is largely a question of understanding the instrumentation assembly and knowing what to look for when some component within the system is malfunctioning. The key ingredient in both maintaining and troubleshooting the system is understanding the individual subsystem functions and approaching both maintenance and troubleshooting in a careful systematic manner.

MAINTENANCE OF A TDU-GC SYSTEM

Several different compressed gases are used with the TDU-GC system and attention should be given to frequently monitoring the tank pressures of these gases. In some situations it would be highly undesirable to deplete one of the gas supplies while a TDU-GC test was being conducted. There is a considerable amount of compressed air consumed by the TDU-GC (for cooling of the reactor inlet and outlet cavities) and consequently it is desirable to have a ready supply.

Most of the gas supplies also have special filters for removing contaminants from the flowpaths prior to entering either the gas chromatograph or the TDU console. For example, the compressed air that is passed through the reactor is filtered to remove traces of oil and water. Again, it is most desirable to maintain a supply of adequate filters for this system. As the TDU-GC requires a sub-ambient column oven chamber for successful operation, considerable quantities of liquid nitrogen are consumed when conducting tests. Figure 45 shows the special transfer tube attached to the back of a Varian gas chromatograph. It is desirable to maintain short transfer paths and also to have the tight connections so there is not a large loss of coolant or head pressure. Again, for good maintenance and also to minimize down time it is desirable to have an ample supply of liquid nitrogen in 160 liter tanks (delivery pressure of 50 to 80 psig). When operating continuously, two of these tanks can be emptied in one week.

Experience has indicated that the gas chromatograph and its associated components basically requires more maintenance than the high-temperature reactor assembly, the furnace, and the TDU instrumentation console. For example, there is a considerable amount of maintenance activities associated with installing different gas chromatographic columns and making attachments to different detection devices. All of these procedures require supplies of chromatographic components such as tubing ferrules, fittings, and other associated chromatographic hardware. The strip chart recorder and chromatographic output terminal also requires maintenance with respect to chart paper and, in general, keeping the various sensitive moving and electrical parts clean and free from dust.

Proper maintenance of a gas chromatograph is important, particularly, when column changes are being made (such as shown in Figure 46), it is necessary to use two wrenches for all of the connecting fittings. This is especially critical where the fused silicia open tubular column connects to the inlet junction just inside the GC oven. This is a very fragile connection and care must be exercised in making gas-tight seals at this location.

Figure 45. Attachment of Liquid Nitrogen Transfer Tube to Gas Chromatograph.

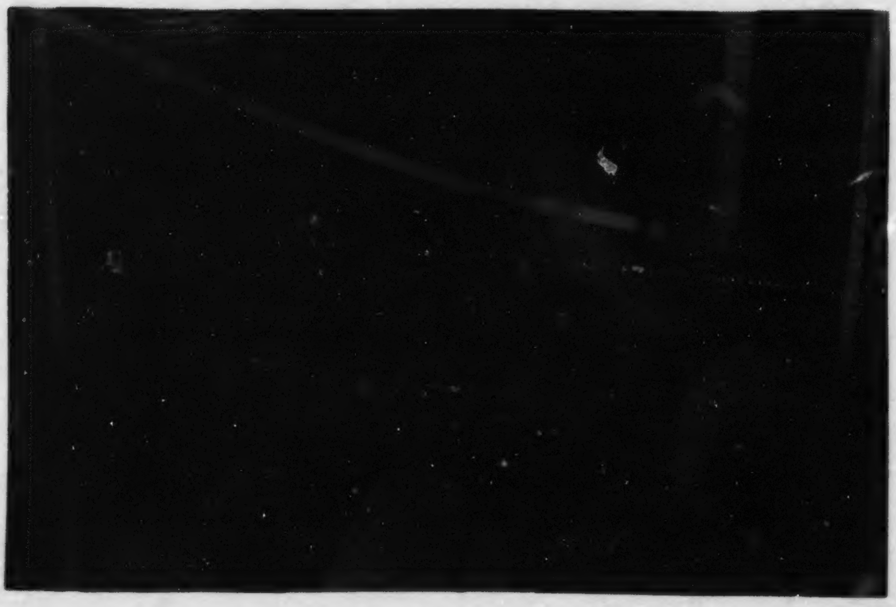


Figure 46. Connecting Fused Silica Column to GC Inlet Tube.

Also, if back-up wrenches are not used at the detector connection, damage can be incurred or leaks can develop in the make-up gas transfer or other parts of the chromatographic flowpath. It is a good practice to perform leak checks on a routine basis.

After connecting a new column to a detector or attaching a column exit to a different detector, it is necessary to establish the proper flows for optimum detector performance. Figure 47 shows a simple procedure for measuring the volumetric gas flow rates at the detector exit. Maintenance problems are minimized if the gas flows to the chromatograph are maintained and only the hydrogen fuel to the hydrogen flame ionization detector should be turned off when the instrument is not being used. The hydrogen gas should be shut off at the gas flow control valve as shown in Figure 48 and not at the supply cylinder. Also, experience has indicated that maintenance problems are minimized if power to the gas chromatograph is left on at all times. However, if the instrument is not being used overnight or over a weekend, it would be best to reduce the temperatures of the oven, the injector, and the detectors. It seems that if power is disconnected from the GC instrument, maintenance problems tend to increase.

Maintenance associated with the TDU portion of the system is relatively minor. It is certainly advisable to check periodically to see if the gas filters are still active. Figure 49 shows the interior of the instrumentation console and the location of a "hydro-purge" filter that is used for drying and removing organic contaminants from incoming air to the TDU-GC. This filter should be checked periodically as should the oxygen removal trap on the inert gas tubing that enters the TDU console.

Very few problems have been associated with the thermoelectric circuits in the TDU as its chromel/alumel thermocouples have been found to exhibit extremely long life even at some of the elevated TDU temperatures. Periodically, the thermocouple connectors at the front end of the TDU console, such as shown in Figure 50, do need to have the contacts cleaned and this is a very simple procedure using fine emery cloth to remove any oxides

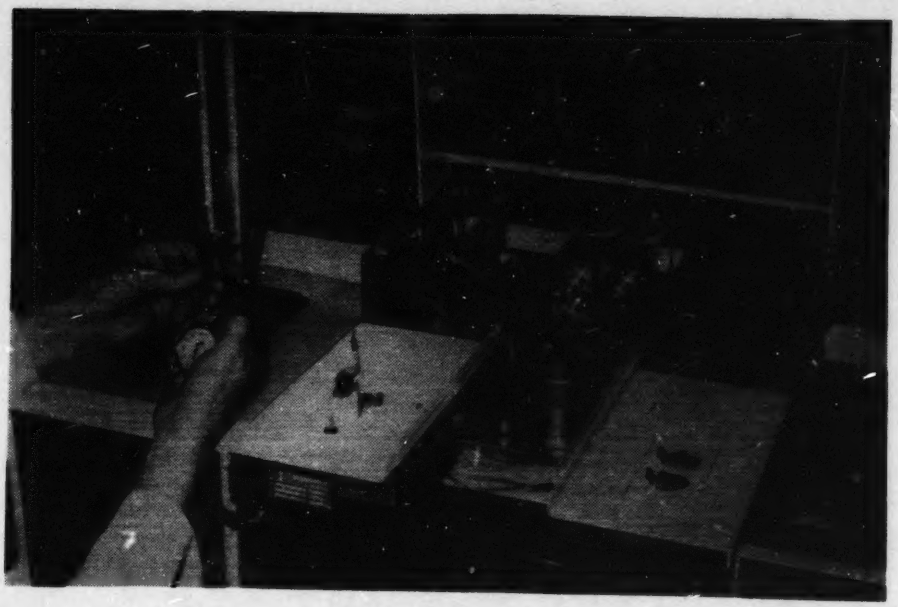


Figure 47. Gas Flow Measurement Procedure.

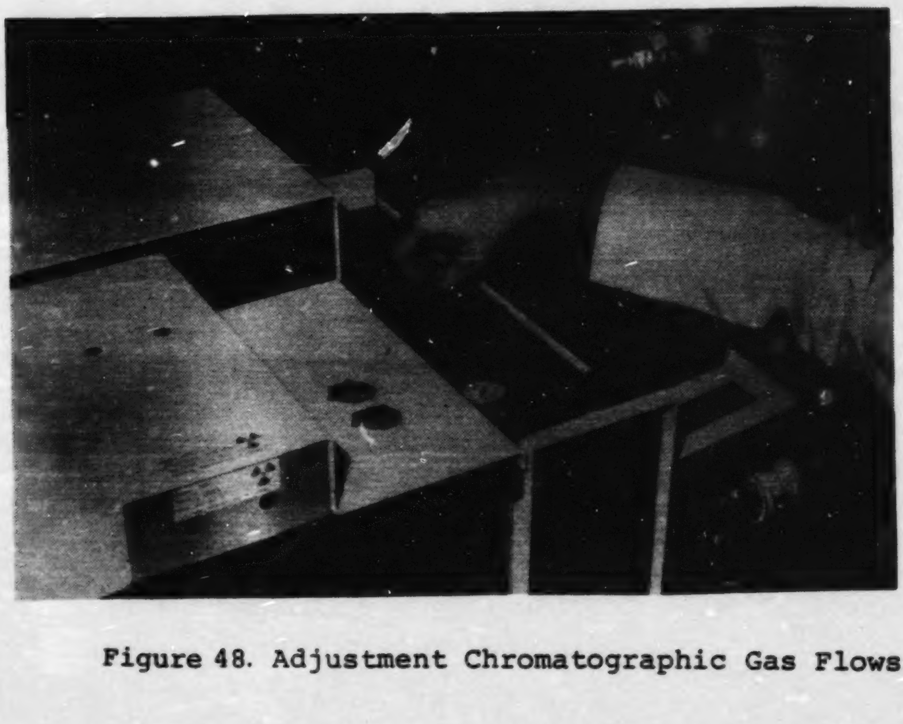


Figure 48. Adjustment Chromatographic Gas Flows.

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Figure 49. Interior View of TDU Instrumentation Console.

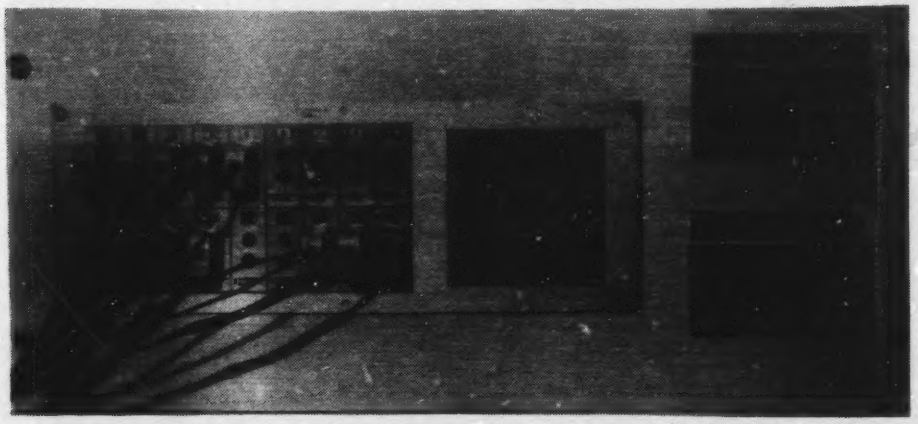

Figure 50. Thermocouple Connectors and Temperature Read Out Devices.

or residue that might have formed on terminal contacts. The electrical heating circuits within the TDU have not presented any problems, however, when some of the electrical controllers have been transported or moved, there have been some associated problems with their performance and reliability. Even so, once these components have been installed in a laboratory setting that is air conditioned and humidity controlled, almost no maintenance problems have occurred.

With respect to the TDU effluent, both the vent from the high-temperature reactor and the glove box vent require frequent changing of the charcoal traps. The spent charcoal should be handled with extreme care and disposed of in a proper manner.

TROUBLESHOOTING A TDU-GC SYSTEM

Component malfunctions in the TDU and in the GC have been relatively rare. Troubleshooting of the gas chromatograph is relatively straight forward and there are numerous troubleshooting procedures that can be used for a gas chromatograph, the potentiometric recorder, and the data processing terminal. If an analyst that is operating the TDU-GC is experiencing difficulties with the gas chromatograph or one of its peripheral components it would be best to consult the troubleshooting section of the manufacturer's instrument manual. Gas chromatographs that are of the modular design often times have diagnostic troubleshooting procedures that accompany the instrument, and in the case of the two chromatographs that have been used with the TDU-GC systems, this is precisely the case. A troubleshooting manual exists for both the Varian 3700 and the Vista 44 system. However, there are instances when the operator of the TDU-GC will probably not be able to diagnose certain difficulties with the gas chromatographic equipment. It will then be necessary to contact the GC manufacturer for further troubleshooting and diagnosing of these more complicated malfunctions, e.g., solid state circuit component failure, integrated circuit malfunctions, or other complicated electronic problems that can not be readily addressed. In most cases, the manufacturer can solve these problems rather quickly by merely changing a circuit board or a modular component of the chromatographic equipment.

With respect to troubleshooting the TDU portion of the TDU-GC system, troubleshooting activities can generally be divided into two distinct classes of problems; one being gas flow or pneumatic difficulties and the other class being electrical malfunction problems. By having ready access to the gas flow control module as shown in Figure 51, it is relatively easy to isolate a given malfunction to some troublesome area or component. As shown in Figure 52 it is a relatively simple matter to monitor the output flows using a simple soap bubble flow meter and often times this straight forward procedure permits the analyst to isolate the trouble area to one given location or component such as a faulty regulator, a leaky tubing connection, and, if the case may be, a cracked or broken high-temperature thermal reactor assembly.

Practically any flowpath component or pneumatic control device can be isolated and its performance readily checked by gas pressurization and output flow measurements. Flow measurements can also be made at the inlet region to the reactor as shown in Figure 53, and they can be very readily made at the outlet of the reactor either before or after the flowpath restrictor.

With respect to the simple electrical problems, the digital VOM that is a key component in a TDU instrumentation console has proven to be an especially valuable tool for troubleshooting activities with the TDU-GC system. By attaching extended leads to this measuring device, it is possible to measure voltages and small currents for practically any of the electrical components within the system. Also, as shown in the photograph of Figure 54, it is an easy matter to troubleshoot for a defective thermocouple, thermocouple connector, or loose electrical connection with the use of the resistance measuring capacity of the digital VOM.

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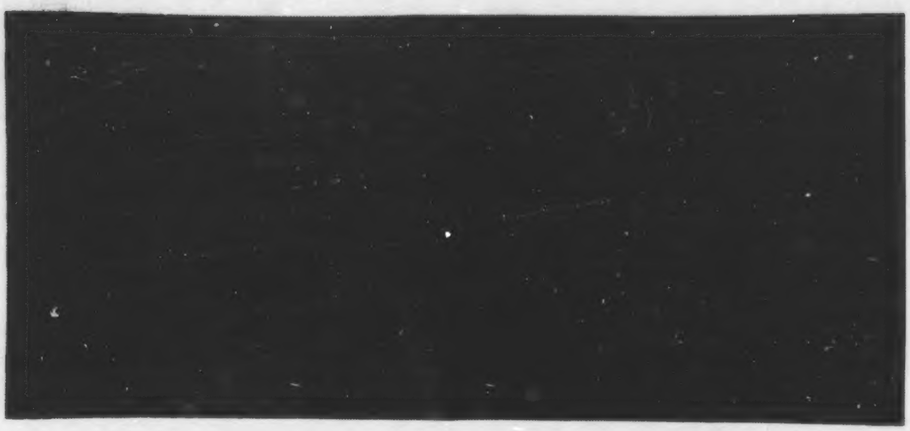

Figure 51. Front View of Gas Flow Control Module.

Figure 52. Flow Measurments at Front End of Console.

Figure 53. Flow Measurements at Inlet Region of Reactor.

Figure 54. Troubleshooting Thermoelectric Circuits.

For the more involved electrical problems that might be encountered in troubleshooting various components of this system, it may be necessary to have the services of an electronics technician to perform some of the more detailed electrical troubleshooting. To assist in these more difficult troubleshooting activities, Appendix A of this report contains detailed schematics of the major electrical components that are included in the TDU-GC system. To make some of these measurements and troubleshoot the more difficult possible problems, the use of an oscilliscope or other special electronic equipment may be required.

The troubleshooting of the TDU-GC system located in the Environmental Chemistry Laboratory at the University of Dayton has not involved any of the highly sophisticated electrical measurements and this unit has been in operation since March of 1982.

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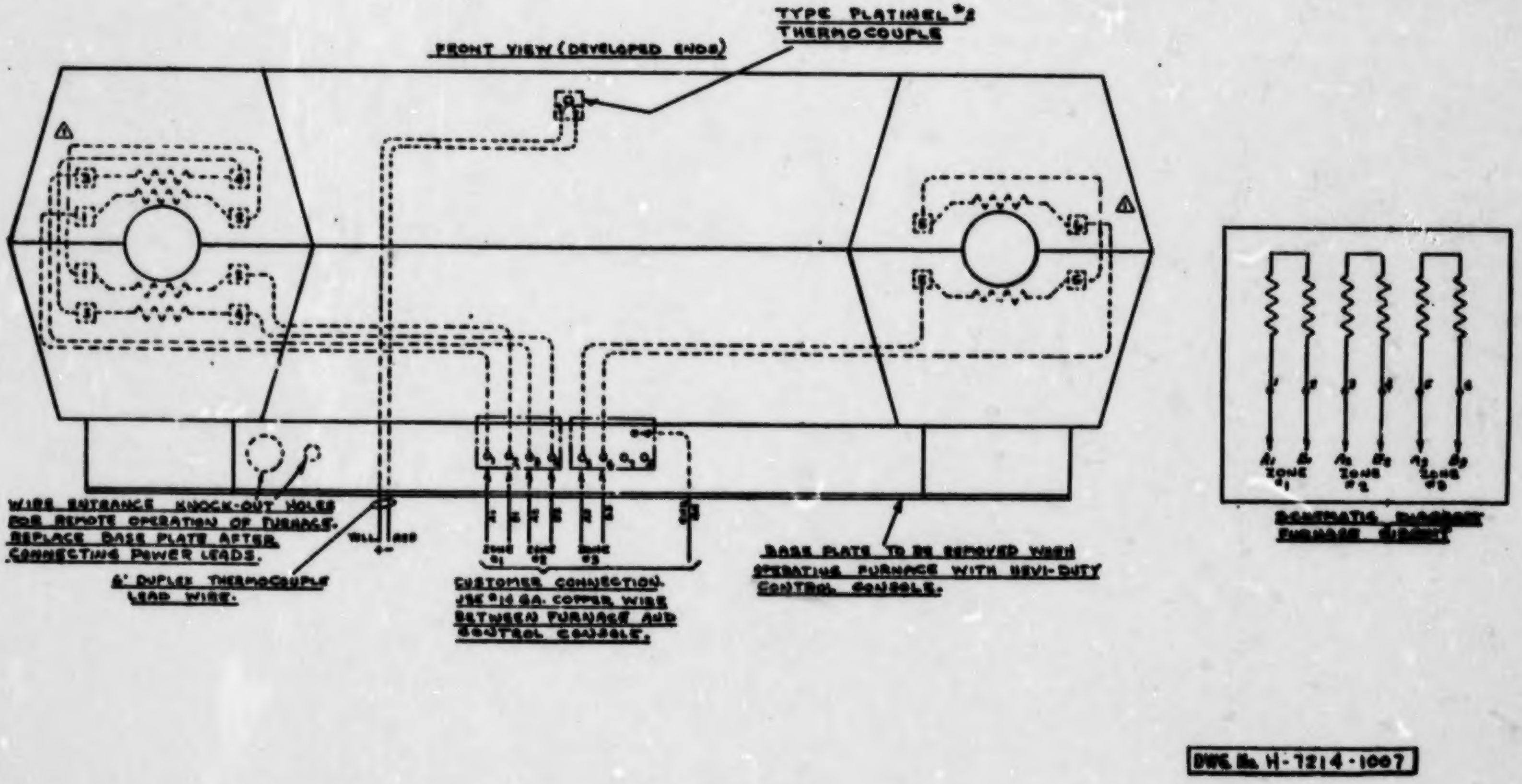
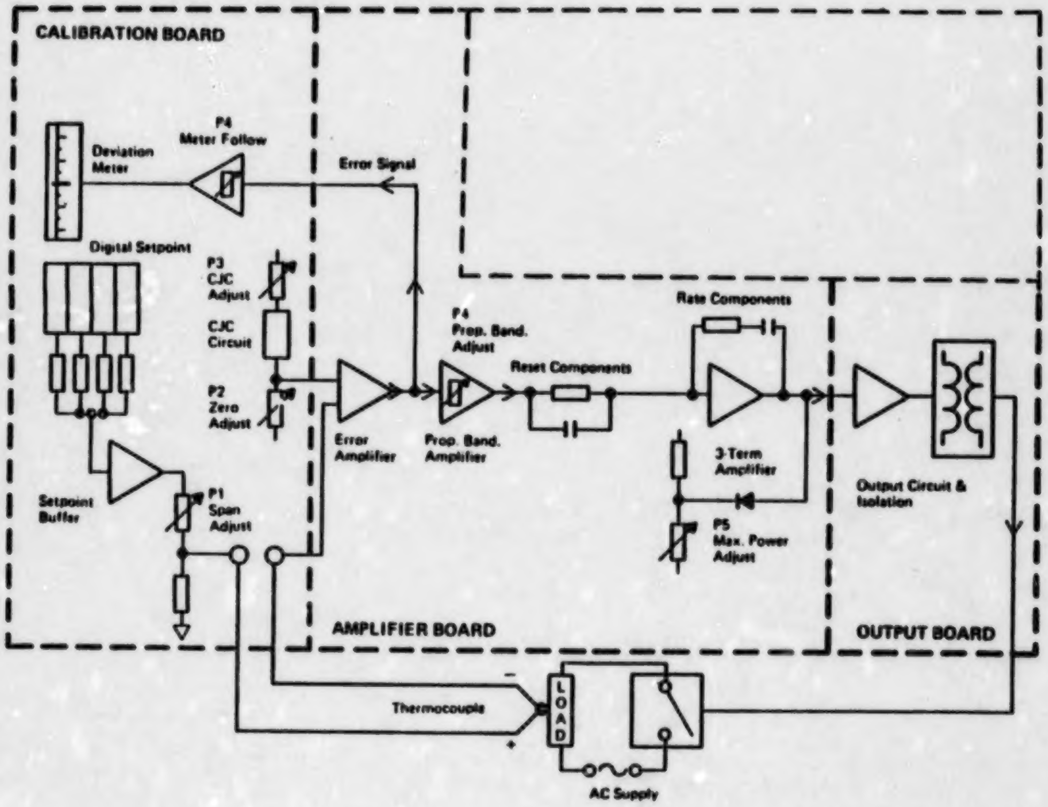
APPENDIX A

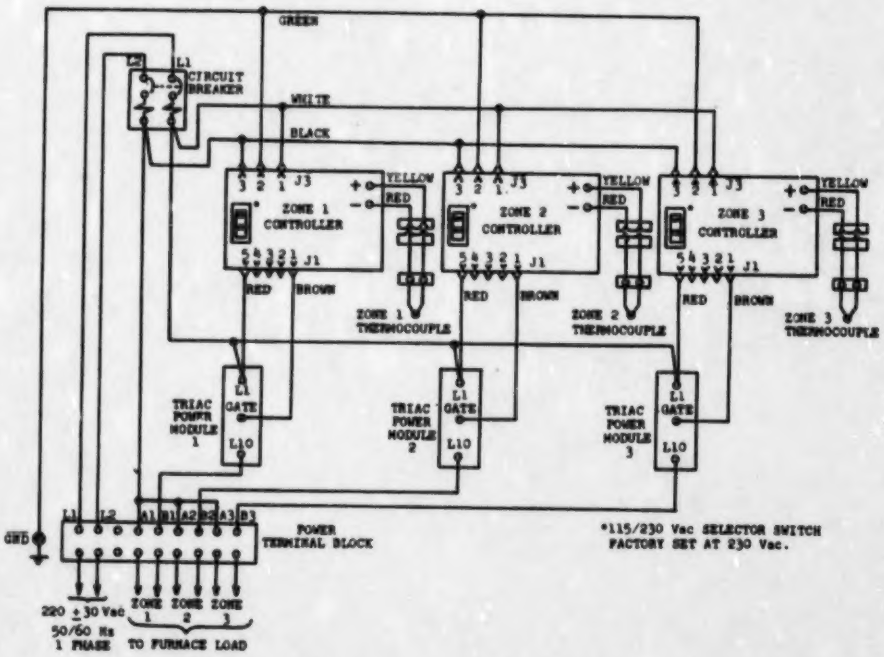
SCHEMATICS OF TDU-GC ELECTRICAL AND ELECTRONIC COMPONENTS


FRONT VIEW (DEVELOPED ENDS)
TYPE PLATINEL #2 THERMOCOUPLE
WIRE ENTRANCE KNOCK-OUT HOLES FOR REMOTE OPERATION OF FURNACE. REPLACE BASE PLATE AFTER CONNECTING POWER LEADS.
6' DUPLEX THERMOCOUPLE LEAD WIRE.
YELL
RED
ZONE #1
ZONE #2
ZONE #3
CUSTOMER CONNECTION. USE #14 GA. COPPER WIRE BETWEEN FURNACE AND CONTROL CONSOLE.
BASE PLATE TO BE REMOVED WHEN OPERATING FURNACE WITH HEVI-DUTY CONTROL CONSOLE.
A1
B1
A2
B2
A3
B3
SCHEMATIC DIAGRAM FURNACE CIRCUIT
DWG. No. H-7214-1007

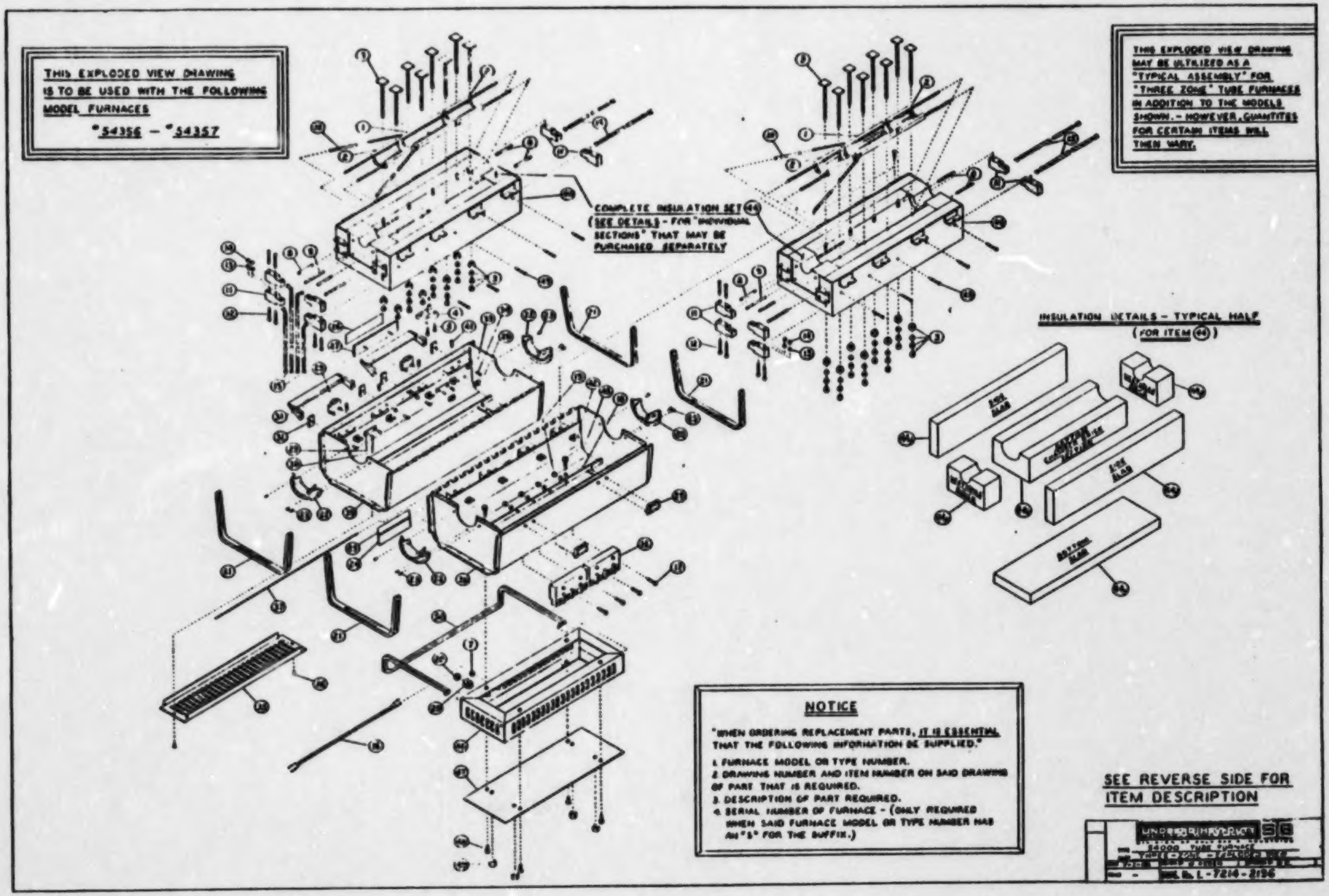
Lindberg Furnace Power Connections.


CALIBRATION BOARD
Deviation Meter
P4 Meter Follow
Error Signal
Digital Setpoint
P3 CJC Adjust
CJC Circuit
P2 Zero Adjust
Setpoint Buffer
P1 Span Adjust
Error Amplifier
P4 Prop. Band. Adjust
Prop. Band. Amplifier
Reset Components
Rate Components
3-Term Amplifier
P5 Max. Power Adjust
Output Circuit & Isolation
AMPLIFIER BOARD
OUTPUT BOARD
Thermocouple
−
+
LOAD
AC Supply

Lindberg Model #1003 Function Block Diagram.


GREEN
WHITE
BLACK
L2
L1
CIRCUIT BREAKER
3 2 1 J3
ZONE 1 CONTROLLER
ZONE 2 CONTROLLER
ZONE 3 CONTROLLER
+
−
YELLOW
RED
5 4 3 2 1 J1
RED
BROWN
ZONE 1 THERMOCOUPLE
ZONE 2 THERMOCOUPLE
ZONE 3 THERMOCOUPLE
TRIAC POWER MODULE 1
TRIAC POWER MODULE 2
TRIAC POWER MODULE 3
L1
GATE
L10
GND
L1 L2 A1 B1 A2 B2 A3 B3
POWER TERMINAL BLOCK
220 ± 30 Vac 50/60 Hz 1 PHASE
ZONE 1 ZONE 2 ZONE 3
TO FURNACE LOAD
*115/230 Vac SELECTOR SWITCH FACTORY SET AT 230 Vac.

Lindberg Models 59744-A and 59754-A Control Consoles Wiring Diagram.


THIS EXPLODED VIEW DRAWING IS TO BE USED WITH THE FOLLOWING MODEL FURNACES
"54356 – "54357

THIS EXPLODED VIEW DRAWING MAY BE UTILIZED AS A "TYPICAL ASSEMBLY" FOR "THREE ZONE" TUBE FURNACES IN ADDITION TO THE MODELS SHOWN. – HOWEVER, QUANTITIES FOR CERTAIN ITEMS WILL THEN VARY.

COMPLETE INSULATION SET (SEE DETAILS – FOR "INDIVIDUAL SECTIONS" THAT MAY BE PURCHASED SEPARATELY

INSULATION DETAILS – TYPICAL HALF
(FOR ITEM 44)

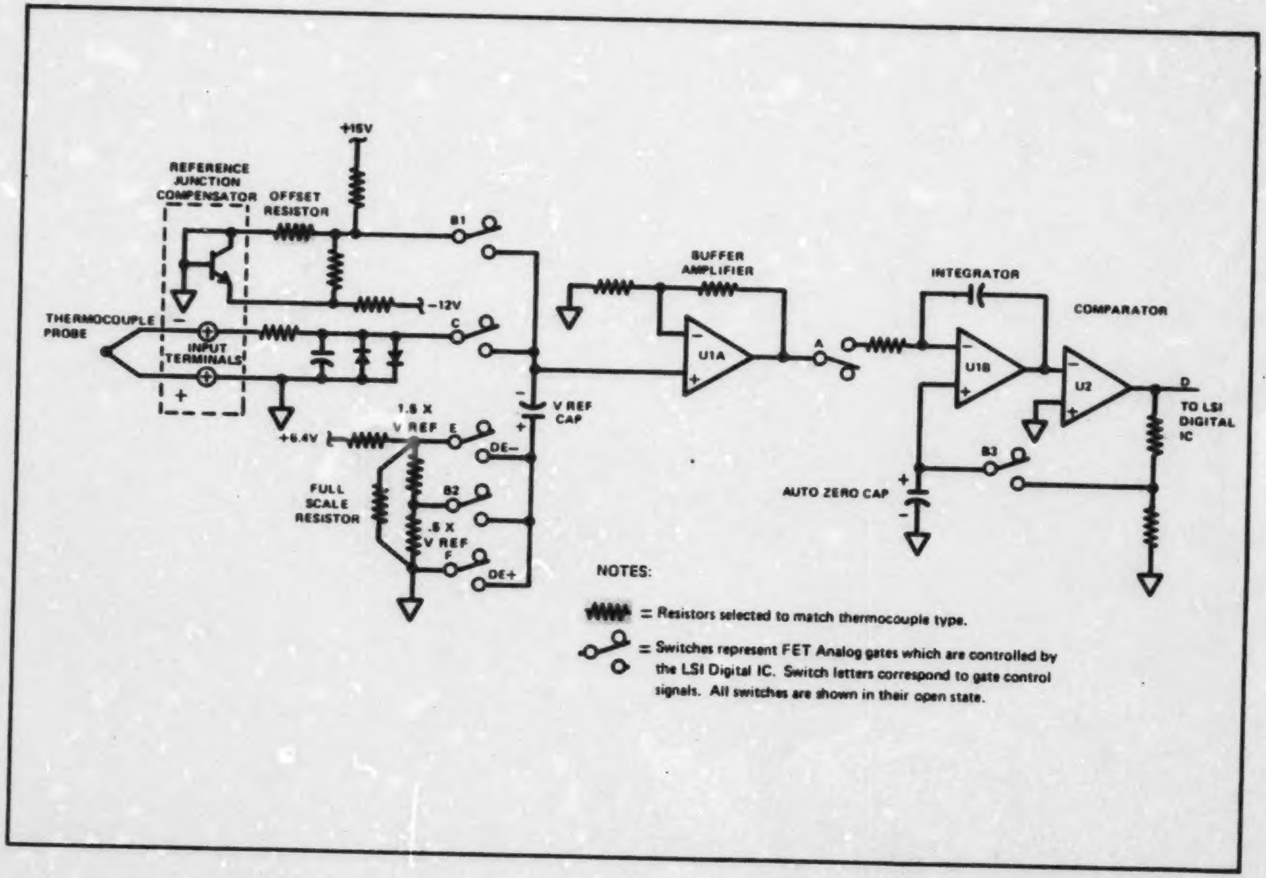
NOTICE

"WHEN ORDERING REPLACEMENT PARTS, IT IS ESSENTIAL THAT THE FOLLOWING INFORMATION BE SUPPLIED."

1. FURNACE MODEL OR TYPE NUMBER.
2. DRAWING NUMBER AND ITEM NUMBER ON SAID DRAWING OF PART THAT IS REQUIRED.
3. DESCRIPTION OF PART REQUIRED.
4. SERIAL NUMBER OF FURNACE – (ONLY REQUIRED WHEN SAID FURNACE MODEL OR TYPE NUMBER HAS AN "S" FOR THE SUFFIX.)

SEE REVERSE SIDE FOR ITEM DESCRIPTION

Exploded View of Lindberg Furnace.

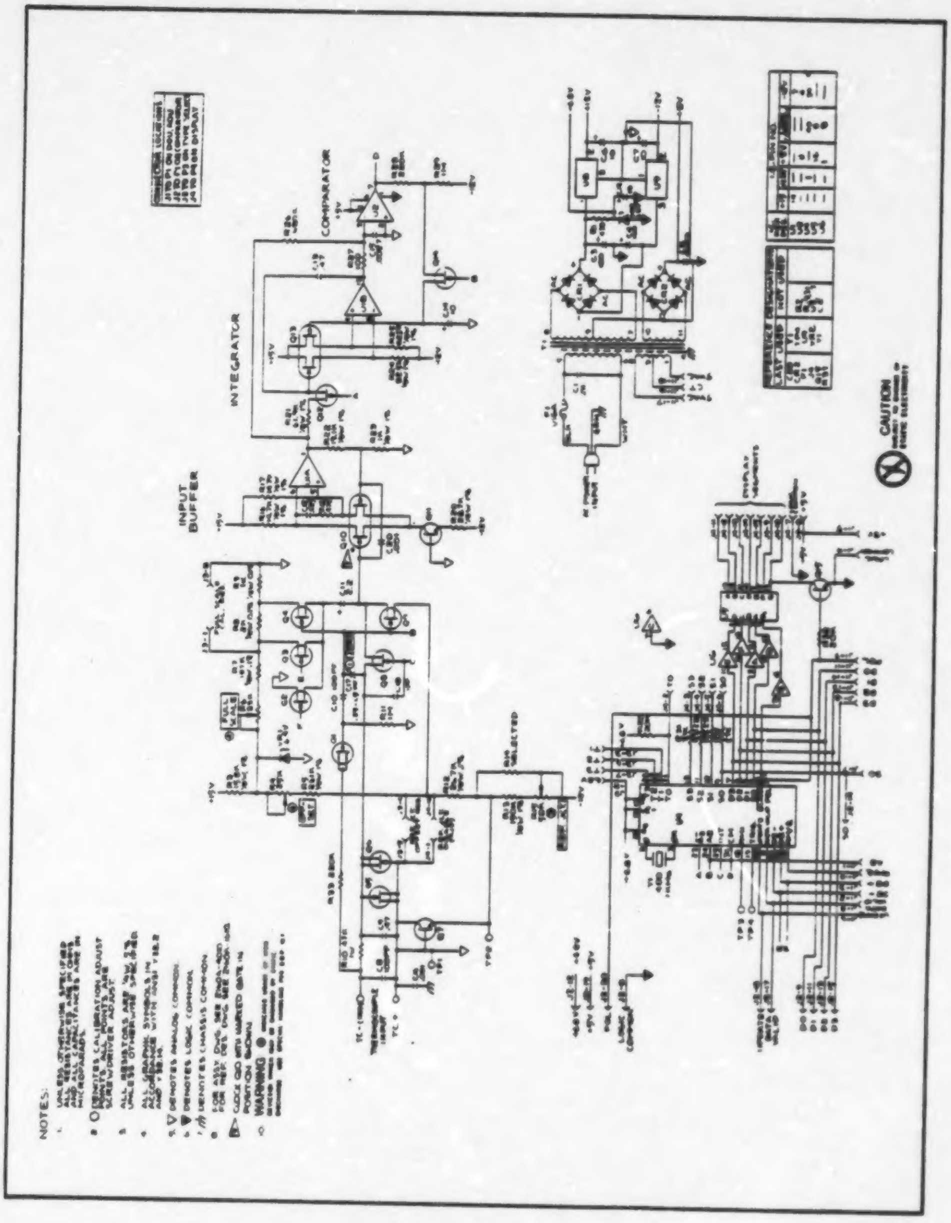

+15V
REFERENCE JUNCTION COMPENSATOR
OFFSET RESISTOR
B1
-12V
THERMOCOUPLE PROBE
INPUT TERMINALS
−
+
C
1.6 X V REF
+6.4V
E
DE−
B2
.8 X V REF
F
DE+
FULL SCALE RESISTOR
V REF CAP
BUFFER AMPLIFIER
U1A
A
INTEGRATOR
U1B
COMPARATOR
U2
D
TO LSI DIGITAL IC
B3
AUTO ZERO CAP

NOTES:

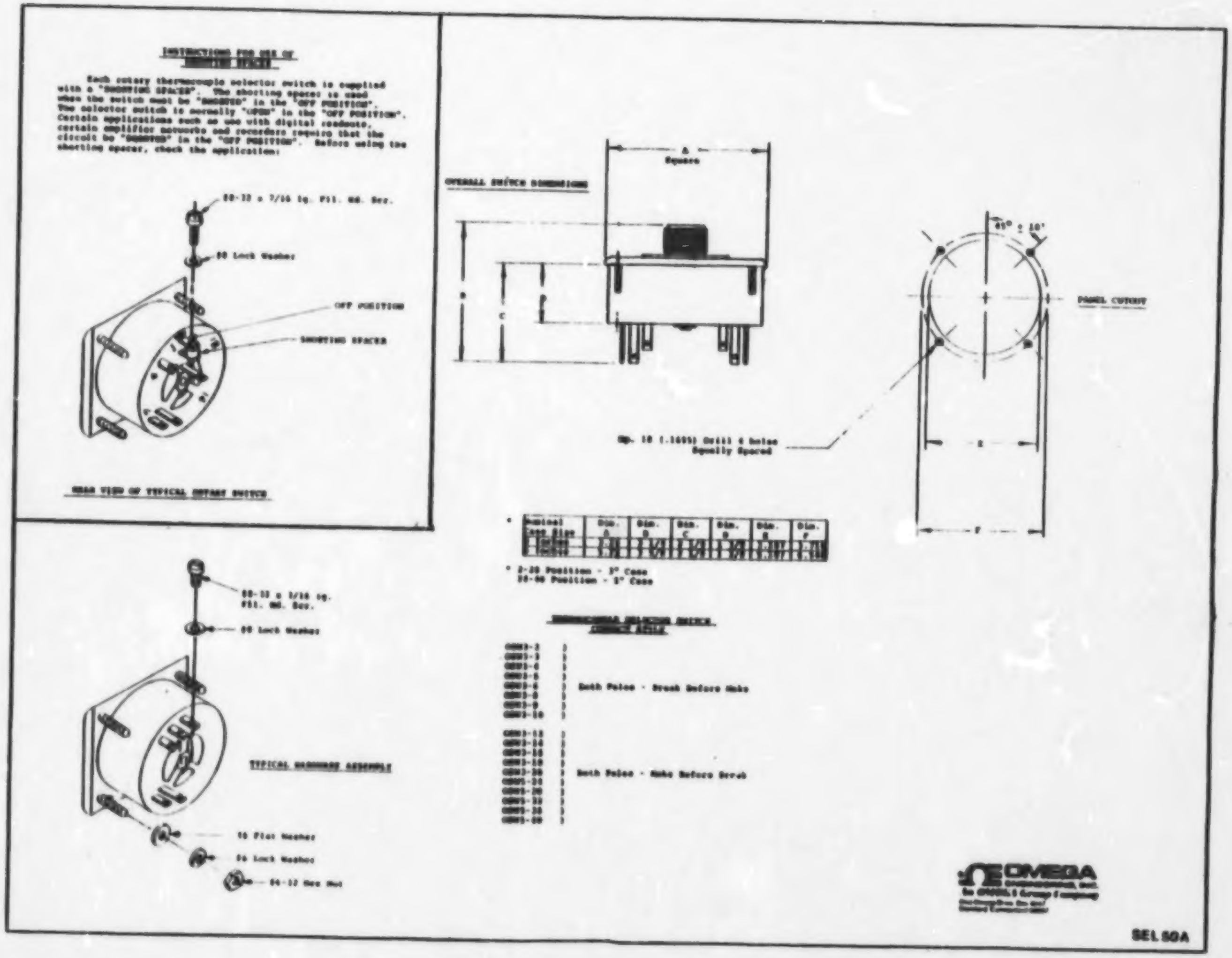
= Resistors selected to match thermocouple type.

= Switches represent FET Analog gates which are controlled by the LSI Digital IC. Switch letters correspond to gate control signals. All switches are shown in their open state.

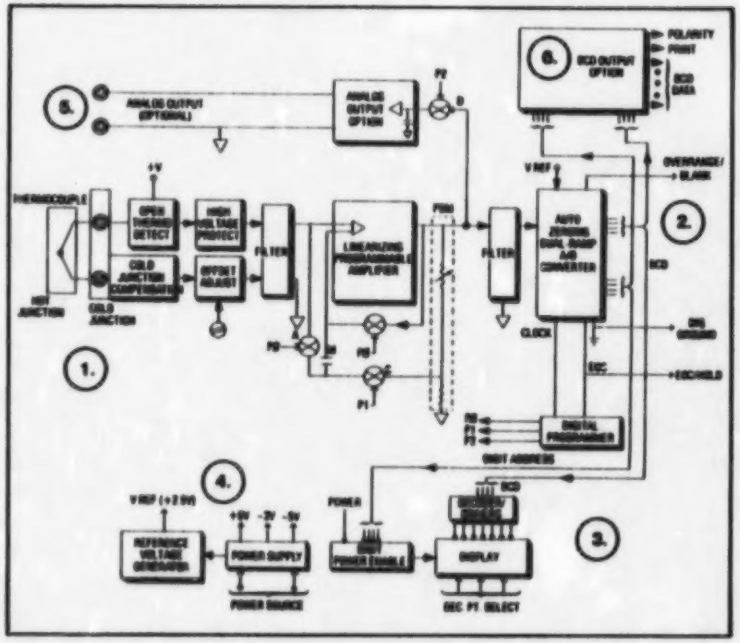
Omega Model 2160A Simplified Schematic.


NOTES:
INPUT BUFFER
INTEGRATOR
COMPARATOR
CAUTION

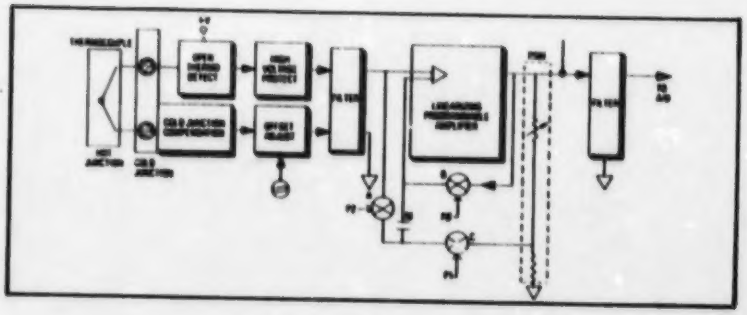
Omega Model 2160A Detailed Schematic.


OFF POSITION
SHORTING SPACER
OVERALL SWITCH DIMENSIONS
A
Square
45° ± 10°
PANEL CUTOUT
Both Poles - Break Before Make
Both Poles - Make Before Break
Flat Washer
Lock Washer
Hex Nut
OMEGA
SEL 50A

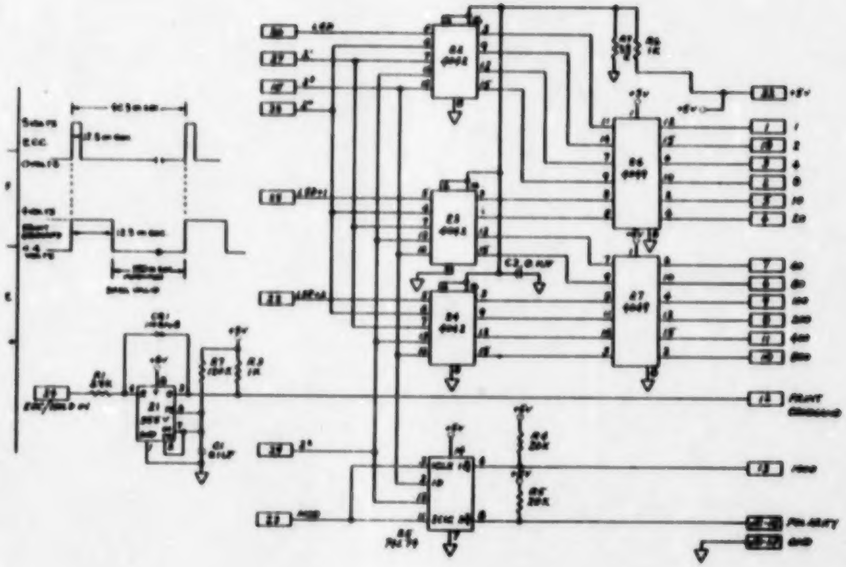
Omega Thermocouple Selector Switch.


5.
ANALOG OUTPUT (OPTIONAL)
ANALOG OUTPUT OPTION
P2
D
6.
BCD OUTPUT OPTION
POLARITY
PRINT
BCD DATA
THERMOCOUPLE
HOT JUNCTION
COLD JUNCTION
+V
OPEN THERMO DETECT
COLD JUNCTION COMPENSATION
HIGH VOLTAGE PROTECT
OFFSET ADJUST
FILTER
LINEARIZING PROGRAMMABLE AMPLIFIER
P0
P0
P1
PGM
FILTER
V REF
AUTO ZEROING DUAL RAMP A/D CONVERTER
OVERRANGE/BLANK
2.
BCD
CLOCK
DIG GROUND
EOC
EOC/HOLD
P0
P1
P2
DIGITAL PROGRAMMER
DIGIT ADDRESS
1.
4.
V REF (+2.0V)
REFERENCE VOLTAGE GENERATOR
+5V
-2V
-5V
POWER SUPPLY
POWER SOURCE
POWER
POWER ENABLE
BCD
DISPLAY
DEC PT SELECT
3.

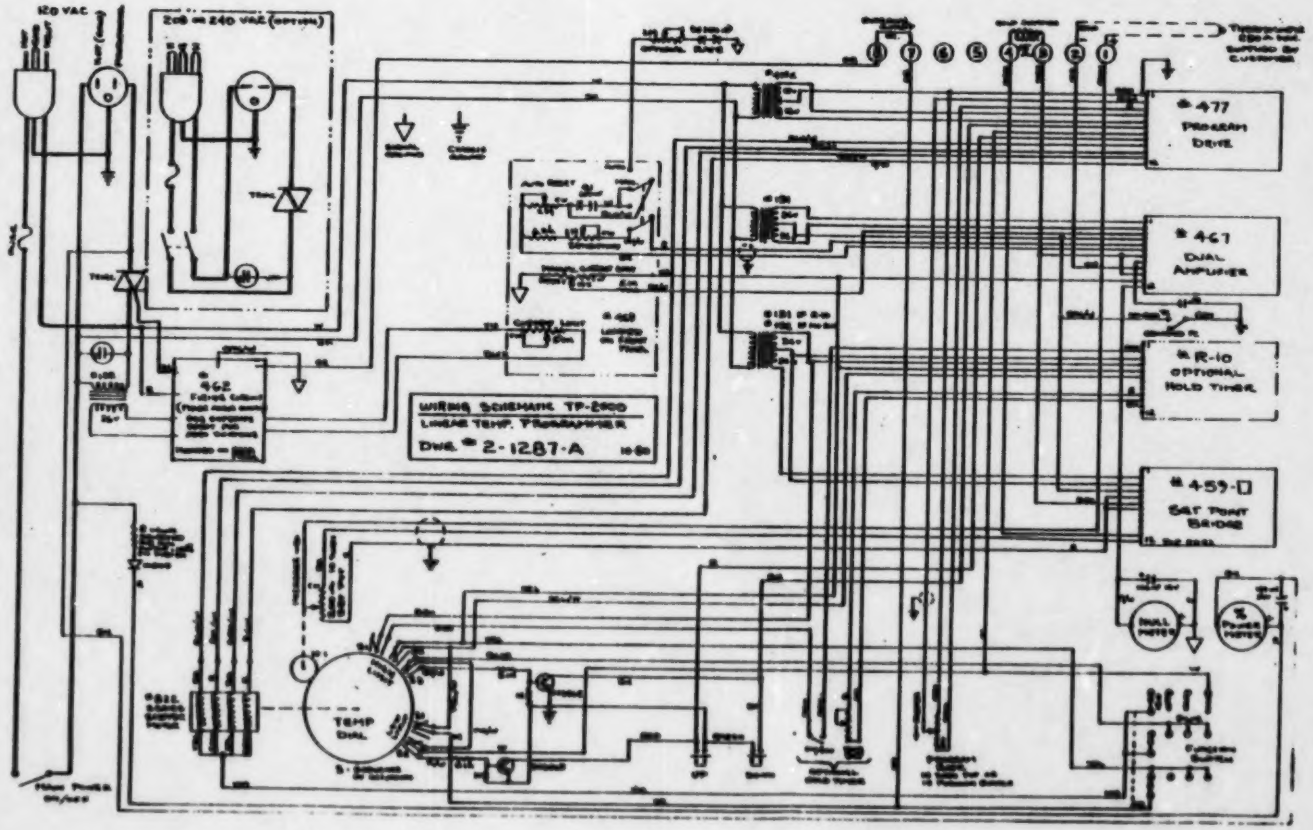
Omega Model 199 Major Functional Block Diagram.


THERMOCOUPLE
HOT JUNCTION
COLD JUNCTION
OPEN THERMO DETECT
HIGH VOLTAGE PROTECT
COLD JUNCTION COMPENSATION
OFFSET ADJUST
FILTER
LINEARIZING PROGRAMMABLE AMPLIFIER
PGM
P1
P2
P3
FILTER

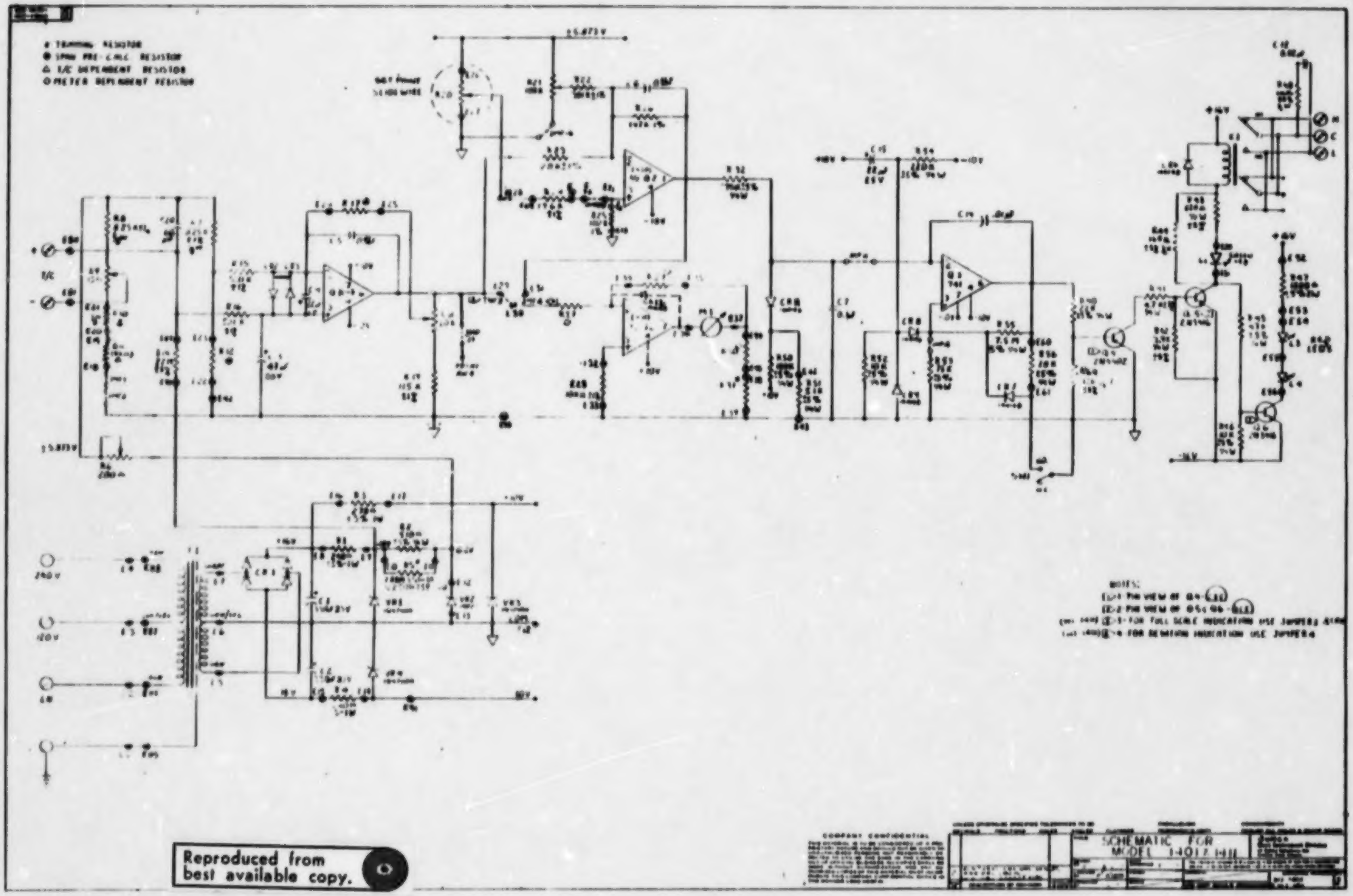
Schematic of Omega Model 199 Signal Conditioning.


+5V
1
2
4
8
10
20
40
80
100
200
400
800
PRINT COMMAND
GND

Omega Model 199 Simplified Schematic.


120 VAC
208 or 240 VAC (OPTION)
# 477 PROGRAM DRIVE
# 461 DUAL AMPLIFIER
# R-10 OPTIONAL HOLD TIMER
# 459-□ SET POINT BRIDGE
# 462
WIRING SCHEMATIC TP-2000
LINEAR TEMP. PROGRAMMER
DWG. # 2-1287-A
TEMP DIAL
NULL METER
% POWER METER
1
2
3
4
5
6
7
8

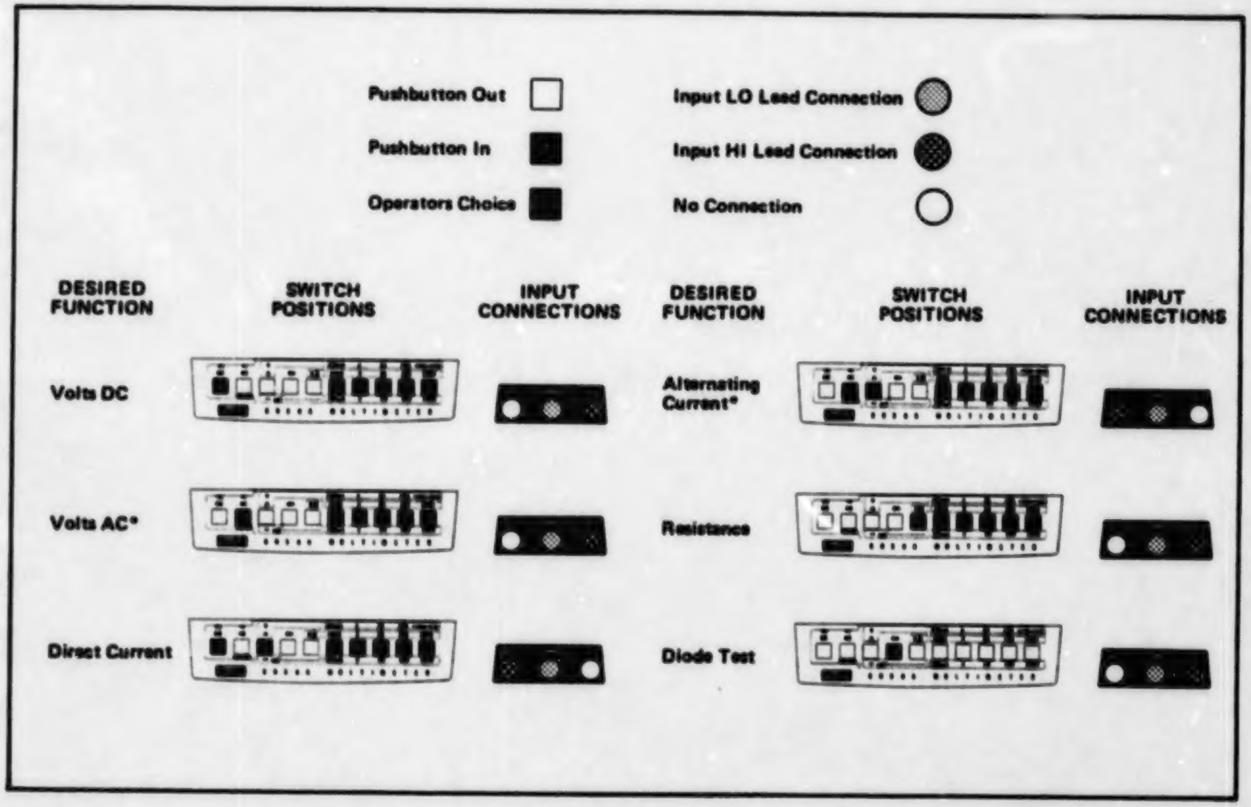
Schematic of TECO TP-2000-T8X-R2-P1-S6 Temperature Programmer.



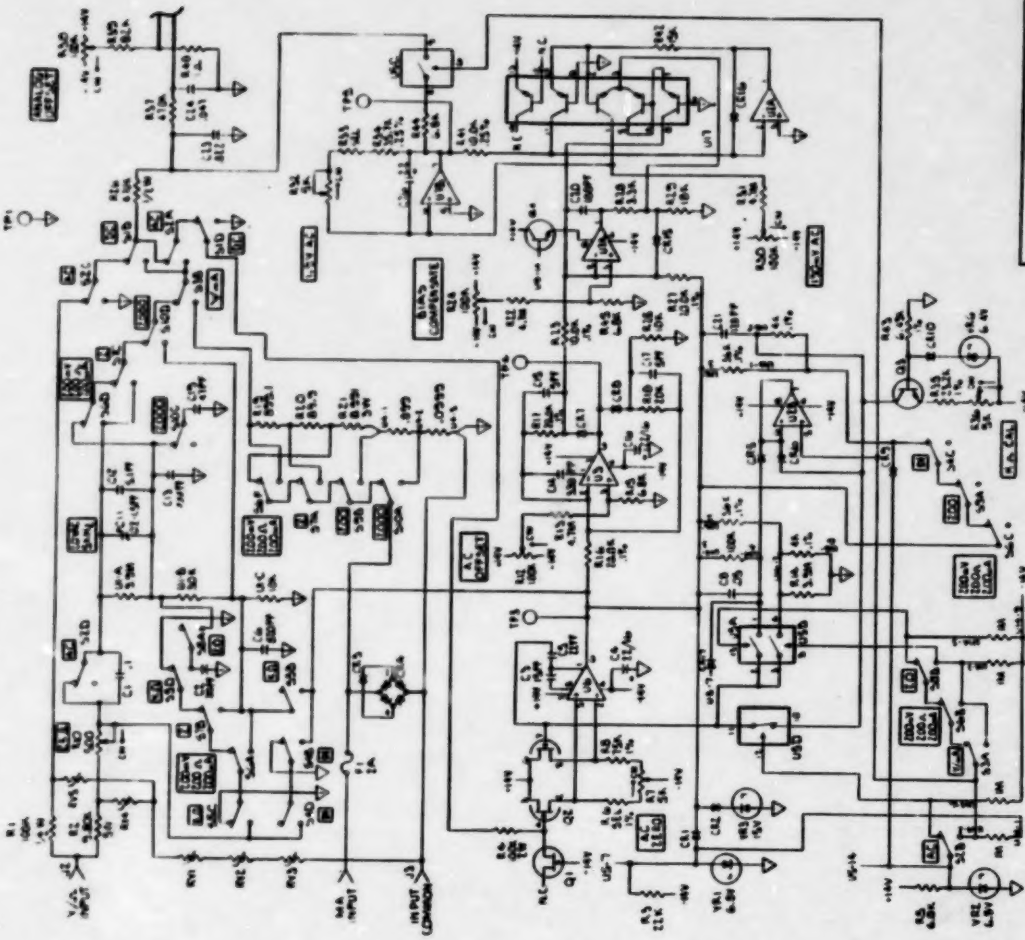
TRIMMING RESISTOR
SPAN PRE-CALC RESISTOR
T/C DEPENDENT RESISTOR
METER DEPENDENT RESISTOR
T/C
240V
120V
NOTES:
FOR FULL SCALE INDICATION USE JUMPERS
FOR DEVIATION INDICATION USE JUMPER 4
COMPANY CONFIDENTIAL
SCHEMATIC FOR
MODEL 1401/1411

Reproduced from
best available copy.

West Model 1401 Temperature Controller.


Pushbutton Out
Pushbutton In
Operators Choice
Input LO Lead Connection
Input HI Lead Connection
No Connection
DESIRED FUNCTION
SWITCH POSITIONS
INPUT CONNECTIONS
DESIRED FUNCTION
SWITCH POSITIONS
INPUT CONNECTIONS
Volts DC
Alternating Current*
Volts AC*
Resistance
Direct Current
Diode Test

Function Selection Examples Using Fluke Model 8030A.



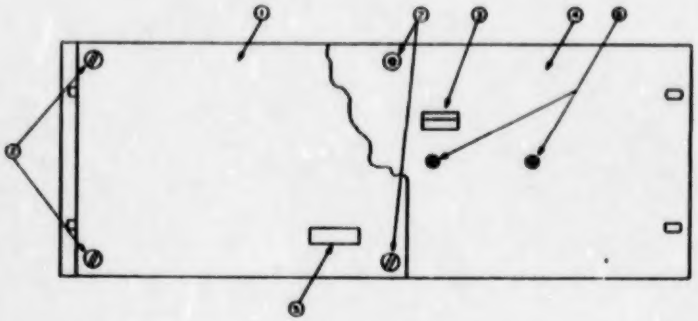
Schematic of Fluke Model 8030A.

Reproduced from best available copy.

APPENDIX B

DETAILS OF FLOW CONTROL MODULE COMPONENTS AND GLOVE BOX ADAPTER

ITEM	DESCRIPTION	DRAWING NO.	NO. REQ'D
1	REAR PANEL	62-EDD-C-007	1
2	6" SPACERS	62-EDD-B-006	4
3	VALVE MOUNT	62-EDD-B-005	1
4	GAS FLOW PANEL	62-EDD-B-003	1
5	FLOW METER MOUNT	62-EDD-B-004	1
6	2.5" SPACERS	62-EDD-B-006	2



UNIVERSITY OF DAYTON RESEARCH INSTITUTE
ENGINEERING DESIGN AND DEVELOPMENT

TITLE ASSEMBLY-GAS FLOW PANEL

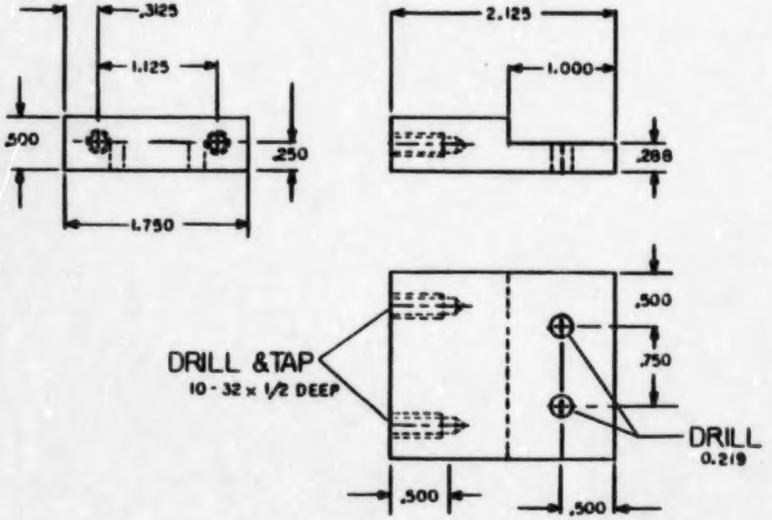
SCALE 1:2

SHEET 1 OF 17

DATE 3-22-62

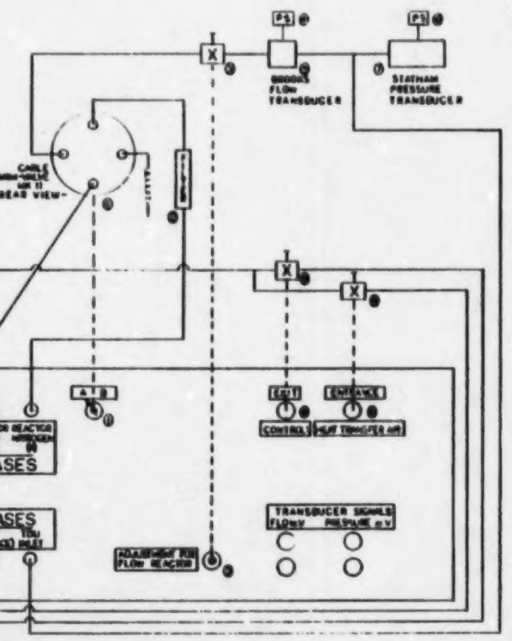
DRAFTSMAN JIM GREEN

DETAIL NO. 82-EDD-C-001


.3125
1.125
.500
.250
1.750
2.125
1.000
.288
DRILL &TAP
10-32 x 1/2 DEEP
.500
.750
DRILL
0.219
.500
.500

DIMENSIONS ARE INCHES

UNIVERSITY OF DAYTON RESEARCH INSTITUTE ENGINEERING DESIGN AND DEVELOPMENT		
TITLE VALVE MOUNT		
MATERIAL ALUMINUM	NO. REQ'D. 1	TOLERANCES
SCALE FULL SIZE	SHEET 5 OF 17	DECIMAL ± FRACTIONS ±
CONTRACT	DATE 2-1-82	ANGLES ±
DRAFTSMAN JIM GREEN	DETAIL NO. 82-EDD-B-005	


PS
PS
BROOKS FLOW TRANSDUCER
STATHAM PRESSURE TRANSDUCER
CARLE MINI-VALVE MV 11 -REAR VIEW-
FILTER
A B
EXIT
ENTRANCE
CONTROL
HEAT TRANSFER AIR
NITROGEN HEAT TRANSFER
REACTOR AIR
REACTOR NITROGEN
INPUT GASES
OUTPUT GASES
NITROGEN
AIR (EXIT)
AIR (ENTRANCE)
TCU INLET
ADJUSTMENT FOR FLOW REACTOR
TRANSDUCER SIGNALS
FLOW mV
PRESSURE mV

ITEM	DESCRIPTION	MODEL NO.	MANUFACTURER
1	Mini-Valve	MV. 11	Carle Instr. Inc. 1200 Knollwood Cr. Anaheim, CA 92801
2	Hydro Purge Filter	Model No. ABC1	Coast Engineering Co. 13568 S. Normandie Ave. Gardena, CA 90249
3	Flow Controller	Model VCD 1000, 0-60CCM	Porter Instr. Co. Hatfield, PA 19440
4	Power Supply	Model 5821-1	Brooks Inst. Div. Emerson Elec. Co. Hatfield, PA 19440
5	Flow Transducer	Model 5810-01C2J4A	Brooks Inst. Div. Emerson Elec. Co. Hatfield, PA 19440
6	Power Supply	Model 01-12-215-01	Sola Electric Co. 1717 Busse Rd. Elk Grove, IL 60007
7	Pressure Transducer	Model P6-15D-350	Statham Laboratories 2230 Statham Blvd. Oxnard, CA 93030
8,9	Metering Valves, Nupro	Model SS-4MA	Whitey Company 5679 Landregan St. Oakland, CA 94662
10	Bulkhead Fittings	Whitey Model SS-200-61	Whitey Company 5679 Landregan St. Oakland, CA 94662

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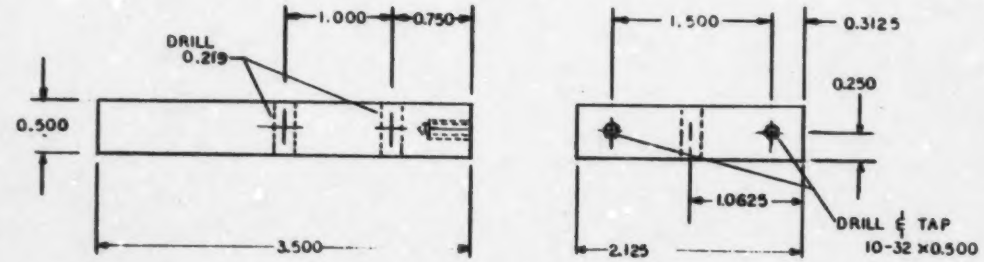
ENGINEERING DESIGN AND DEVELOPMENT

TITLE PLUMBING FOR AIR-GAS FLOW PANEL		
MATERIAL	NO. REQ'D 1	TOLERANCES
SCALE 1/2	SHEET 2 OF 17	DECIMAL ±
CONTRACT	DATE 3-16-82	FRACTIONS ± ANGLES ±
DRAFTSMAN JIM GREEN	DETAIL NO. 82-EDD-C-002	


1.000
0.750
DRILL
0.219
0.500
3.500
1.500
0.3125
0.250
1.0625
DRILL & TAP
10-32 ×0.500
2.125

DIMENSIONS ARE INCHES

UNIVERSITY OF DAYTON RESEARCH INSTITUTE
ENGINEERING DESIGN AND DEVELOPMENT

TITLE
FLOW METER MOUNT

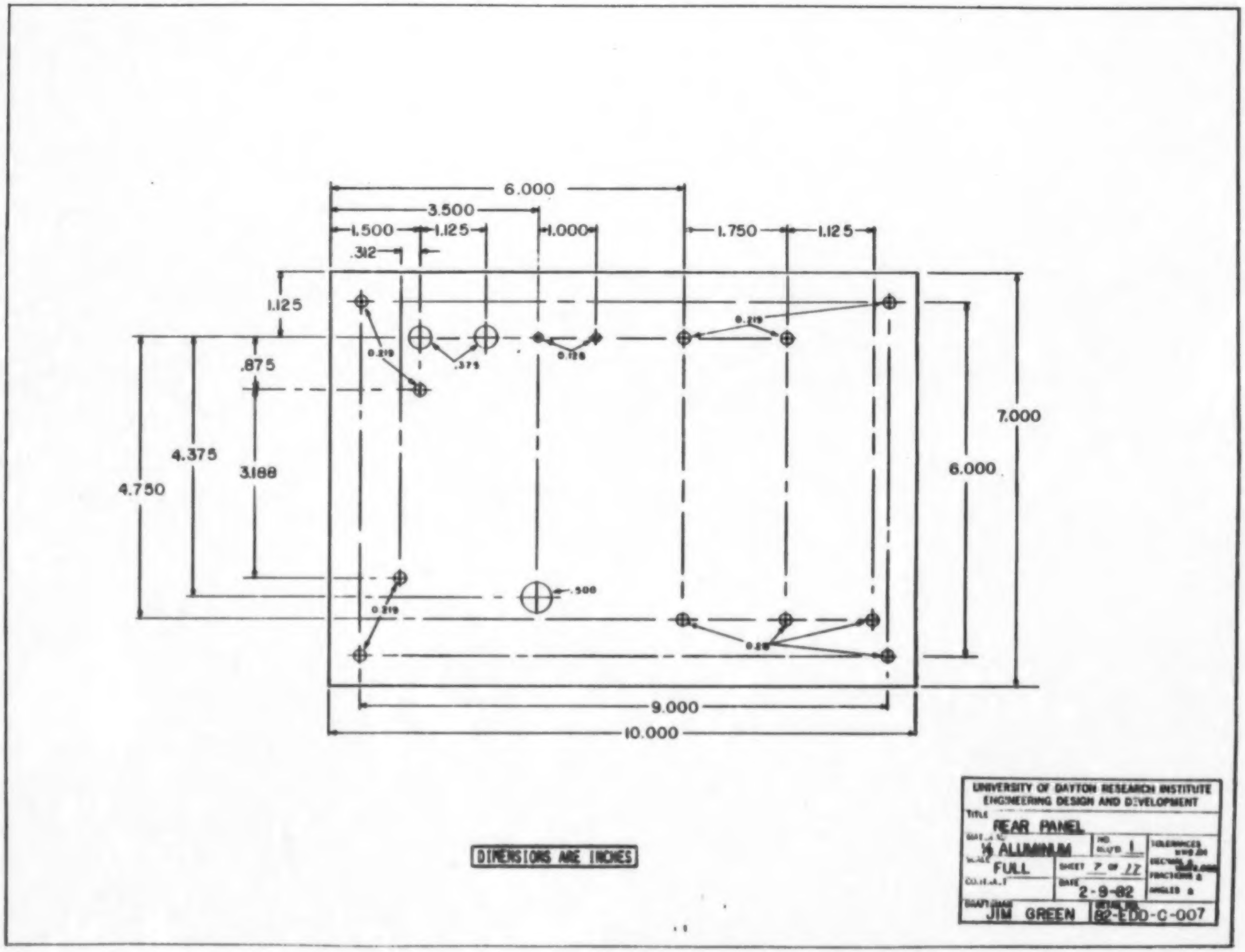
ALUMINUM
1

SCALE
FULL
4 17
±.005

2-8-82

DRAFTSMAN
JIM GREEN

DETAIL NO.
82-EDD-B-004


6.000
3.500
1.500
1.125
1.000
1.750
1.125
.312
1.125
.875
4.375
3.188
4.750
7.000
6.000
9.000
10.000
0.219
.375
0.126
0.219
0.219
.500
0.219
DIMENSIONS ARE INCHES

UNIVERSITY OF DAYTON RESEARCH INSTITUTE
ENGINEERING DESIGN AND DEVELOPMENT

TITLE REAR PANEL

¼ ALUMINUM

NO. REQ'D 1

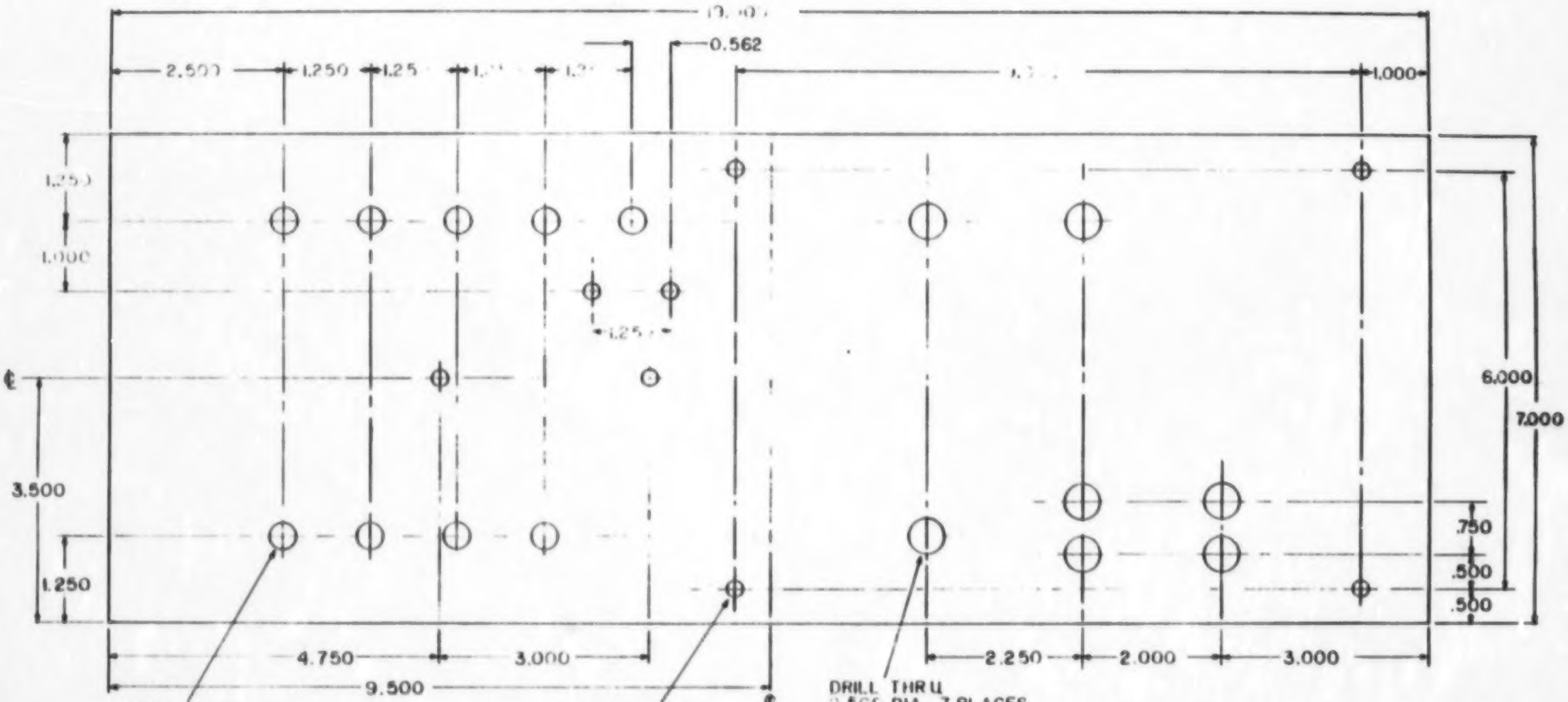
SCALE FULL

SHEET 7 OF 11

DATE 2-9-82

DRAFTSMAN JIM GREEN

82-EDD-C-007


2.500
1.250
1.25
0.562
1.000
1.250
1.000
.125
3.500
1.250
4.750
3.000
9.500
2.250
2.000
3.000
.750
.500
.500
6.000
7.000

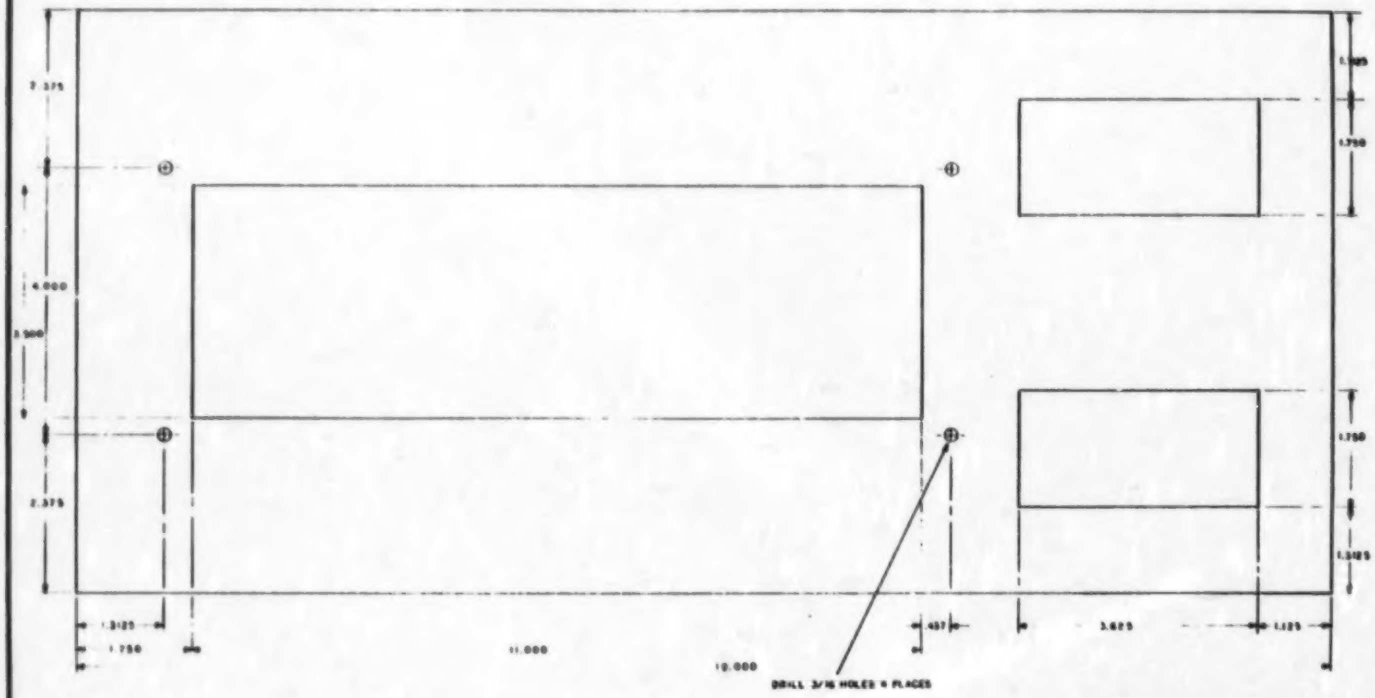
DRILL THRU
0.375 DIA., 9 PLACES

DRILL THRU
0.219 DIA., 8 PLACES

DRILL THRU
0.500 DIA., 7 PLACES

DIMENSIONS ARE INCHES

Reproduced from
best available copy.


2.375
4.000
3.500
2.375
1.3125
1.750
11.000
12.000
.437
3.625
1.125
1.125
1.750
1.750
1.3125
DRILL 3/16 HOLES 4 PLACES

DIMENSIONS ARE INCHES

UNIVERSITY OF DAYTON RESEARCH INSTITUTE
ENGINEERING DESIGN AND DEVELOPMENT

TITLE TEMPERATURE INDICATOR PANEL

MATERIAL BUD 1/8 ALUM

SCALE FULL

SHEET 9 OF 12

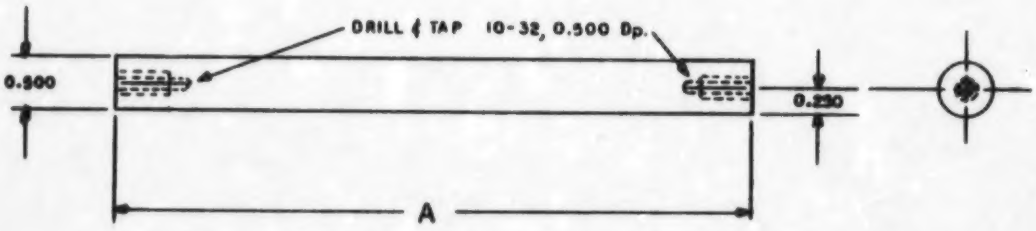
CONTRACT

DATE 3-11-82

ANGLES ±

DRAFTSMAN JIM GREEN

DETAIL NO. 82-EDD-C-009


DRILL & TAP 10-32, 0.500 Dp.
0.500
0.230
A

DIM. A	NO. REQ'D
6.0	4
2.5	2

DIMENSIONS ARE INCHES

UNIVERSITY OF DAYTON RESEARCH INSTITUTE
ENGINEERING DESIGN AND DEVELOPMENT
TITLE SPACERS
ALUMINUM
FULL
6 OF 17
2-9-82
TOLERANCES XX ±.01
DECIMAL ± XXX ±.005
FRACTIONS ±
ANGLES ±
DRAFTSMAN JIM GREEN
DETAIL NO. 82-EDD-B-006

VARIABLE CONSTANT DIFFERENTIAL FLOW CONTROLLERS
MODEL VCD1000

PORTER
INSTRUMENT
COMPANY
HATFIELD PA
MODEL VCD 1000
FLOW CONTROLLER

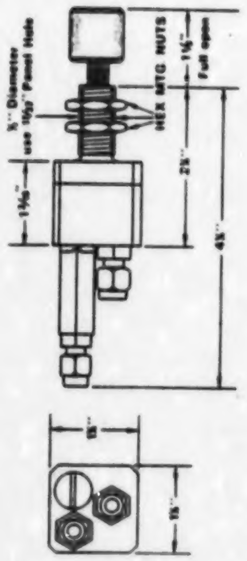
Designed for use in analytical instruments or other applications to control low gas flows at constant mass flow rates regardless of change in downstream pressure. This controller maintains a preset pressure differential across a laminar flow element with the result that the flow output is linear with relation to stem turns. With constant upstream pressure, flow is varied by changing the ΔP across the laminar flow element. This change in differential pressure is accomplished by changing the spring force exerted on the diaphragm with a fine-pitched screw adjustment. Once set, this ΔP is maintained regardless of downstream variations.

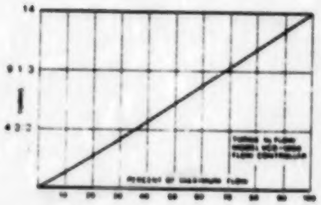
Turns vs. flow relationship is linear.

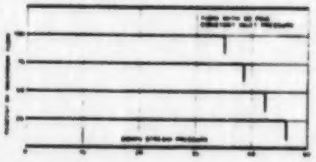
Flow control ranges from 1 cc/min to 400 cc/min are available in a single unit by simply changing the color coded laminar flow element. No special tools are required.

Bubble-tight shut-off is accomplished at the internal control valve insuring that the diaphragm is not pressurized from one side only.

Standard unit includes a replaceable inlet filter.



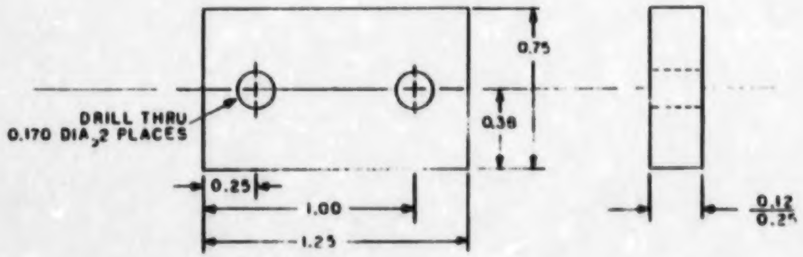




(Helium at 50 psig inlet)

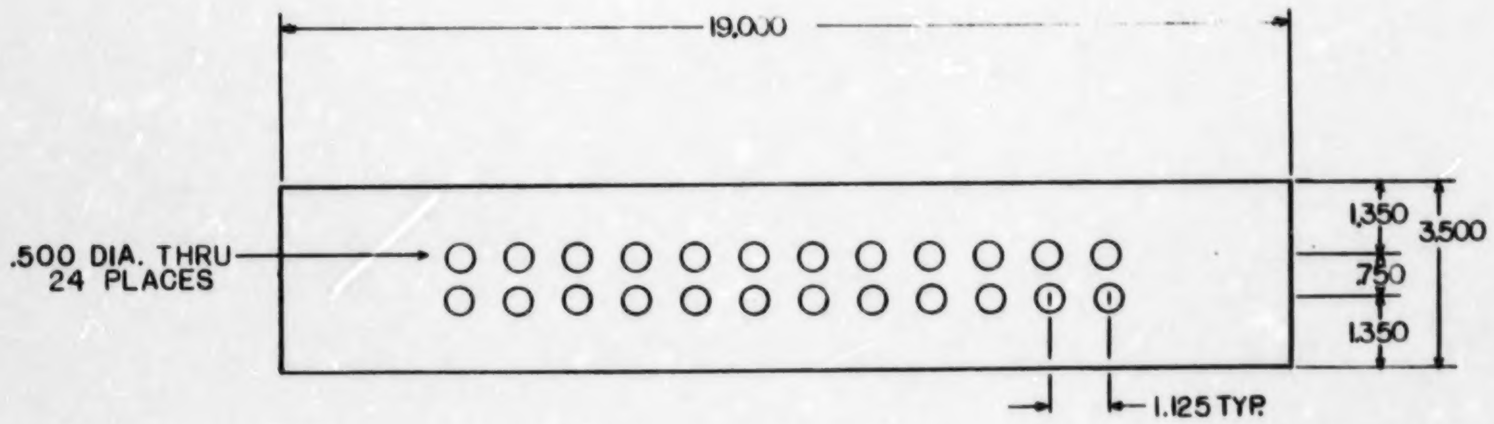
Range	Element Number	Color Code
0.5 - 5.0 cc/min	A-5	Red or Gold
1.0 - 10.0 cc/min	A-10	Blue
6.0 - 60.0 cc/min	A-60	Red
10.0 - 110.0 cc/min	A-110	Green
18.0 - 180.0 cc/min	A-180	Silver
40.0 - 400.0 cc/min	A-400	Black

Precise Flow Control Valve (Porter Instruments VCD 1000,A-60).


DRILL THRU
0.170 DIA, 2 PLACES
0.75
0.38
0.25
1.00
1.25
0.12
0.25

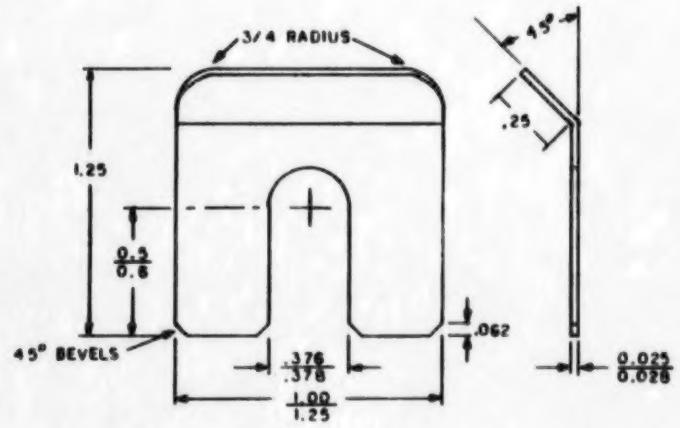
DIMENSIONS ARE INCHES

UNIVERSITY OF DAYTON RESEARCH INSTITUTE
ENGINEERING DESIGN AND DEVELOPMENT
TITLE CARRIER GAS CLAMP
MATERIAL ACRYLIC PLASTIC
NO. REQ'D. 1
TOLERANCES
SCALE 2:1
SHEET 13 OF 17
DECIMAL ± .XX ±.01
FRACTIONS ±
CONTRACT
DATE 3-16-82
ANGLES ±
DRAFTSMAN JIM GREEN
DETAIL NO. 82-EDD-B-013


19,000
1,350
.750
1.350
3,500
.500 DIA. THRU
24 PLACES
1.125 TYP.

DIMENSIONS ARE INCHES

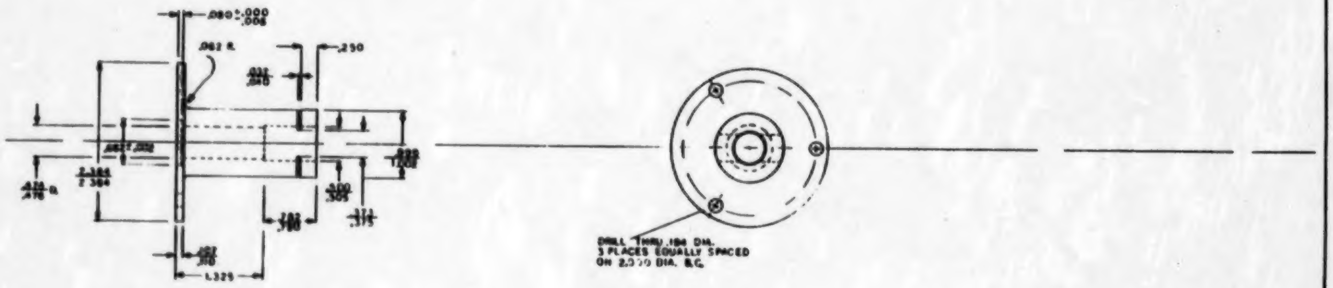
UNIVERSITY OF DAYTON RESEARCH INSTITUTE ENGINEERING DESIGN AND DEVELOPMENT		
TITLE ELECTRICAL INPUT/OUTPUT PANEL		
STOCK 3½ x 19 RACK PANEL	NO. REQ'D. ___	TOLERANCES XX.01 DECIMAL ± XXX.005 FRACTIONS ± ANGLES ±
SCALE 1:2	SHEET 11 OF 12	
CONTRACT	DATE 1-27-82	
DRAFTSMAN JIM GREEN	DETAIL NO. 82-EDD-B-OM	


3/4 RADIUS
45°
.25
1.25
0.5
0.6
45° BEVELS
.062
.376
.378
1.00
1.25
0.025
0.028

DIMENSIONS ARE INCHES

UNIVERSITY OF DAYTON RESEARCH INSTITUTE
ENGINEERING DESIGN AND DEVELOPMENT

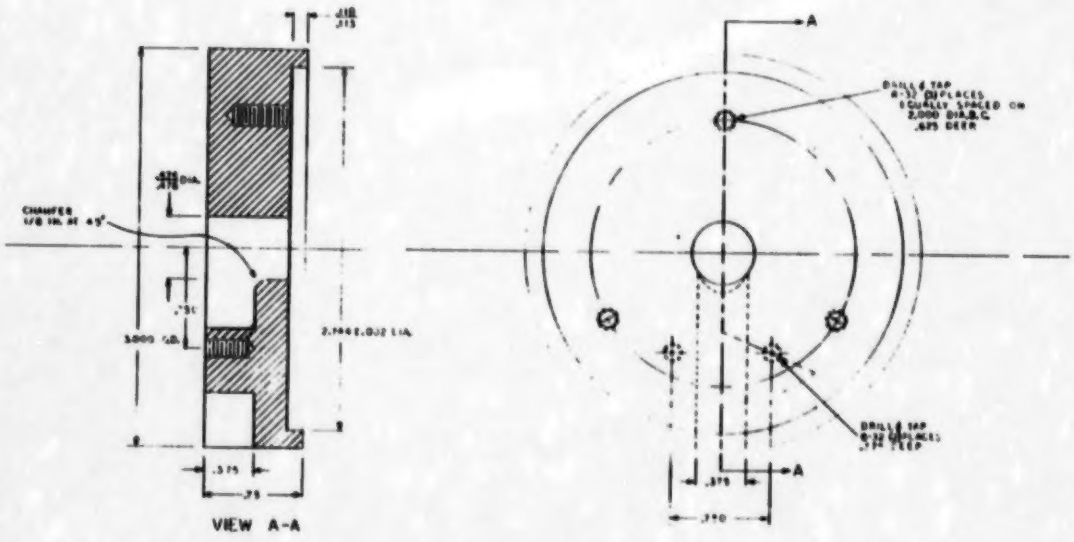
TITLE SAMPLE TUBE LOCKING CLIP
MATERIAL 304 S.S.
NO. REQ'D. 1
TOLERANCES XXX±.005
DECIMAL ±
FRACTIONS ±
ANGLES ±
SCALE 2:1
SHEET 12 OF 17
CONTRACT
DATE 3-19-82
DRAFTSMAN JIM GREEN
DETAIL NO. 82-EDD-B-012


.080 +.000 -.005
.062 R.
.250
2.385
2.384
L.325
.300
.305
DRILL THRU .184 DIA.
3 PLACES EQUALLY SPACED
ON 2.3?0 DIA. B.C.

DIMENSIONS ARE INCHES

UNIVERSITY OF DAYTON RESEARCH INSTITUTE
ENGINEERING DESIGN AND DEVELOPMENT

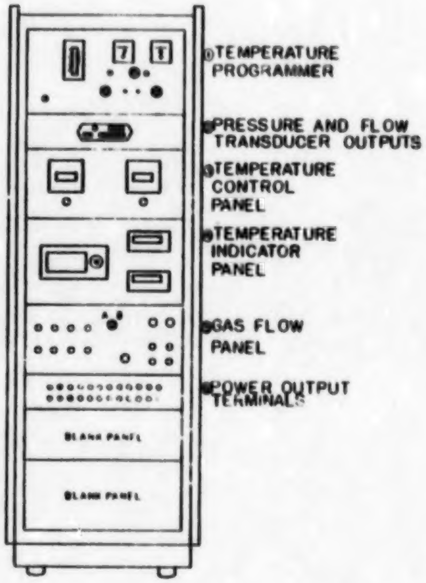
TITLE FRONT GLOVE BOX SEAL		
MATERIAL ACRYLIC PLASTIC	NO. REQ'D. 1	
SCALE FULL	SHEET 14 OF 17	
CONTRACT	DATE 4-14-82	ANGLES ±
DRAFTSMAN J. GREEN	DETAIL NO. 82-EDD-C-014	



.218
.213
.438 DIA.
CHAMFER 1/8 IN. AT 45°
.750
3.000 O.D.
2.744±.002 DIA.
.375
.75
VIEW A-A
A
A
DRILL & TAP 8-32 (3) PLACES EQUALLY SPACED ON 2.000 DIA.B.C. .625 DEEP
DRILL & TAP 8-32 (2) PLACES .375 DEEP
.375
.790

DIMENSIONS ARE INCHES

UNIVERSITY OF DAYTON RESEARCH INSTITUTE
ENGINEERING DESIGN AND DEVELOPMENT
REAR GLOVE BOX SEAL
ACRYLIC PLASTIC
1
2:1
4-15-82
J. GREEN
82-EDD-C-015


①TEMPERATURE PROGRAMMER
②PRESSURE AND FLOW TRANSDUCER OUTPUTS
③TEMPERATURE CONTROL PANEL
④TEMPERATURE INDICATOR PANEL
⑤GAS FLOW PANEL
⑥POWER OUTPUT TERMINALS
7
T
BLANK PANEL
BLANK PANEL

① THEALL ENG.CO., OXFORD, PA.
NO. TP-2000-5" PANEL

② FLUKE MULTIMETER
NO. 8030A-1 1/2 PANEL

③ WEST TEMPERATURE CONTROLLERS
NO. 1402-0 TYPE K, 7" PANEL 0-600°

④ OMEGA TEMPERATURE INDICATOR
NO. 199 TYPE K
OMEGA TEMPERATURE INDICATOR
NO. 2160A, TYPE K
OMEGA THERMOCOUPLE SWITCH PANEL
NO. HTC-03JP1-10-10K
NO. HTC-05M3-10-SWITCH
DRWG. NO. 82-EDD-C-008 8 3/4" PANEL

⑤ GAS FLOW
DRWG. NO. 82-EDD-B-003
7" PANEL

⑥ ELECTRICAL INPUT/OUTPUT PANEL
DRWG. NO. 82-EDD-B-011 3 1/2" PANEL

UNIVERSITY OF DAYTON RESEARCH INSTITUTE
ENGINEERING DESIGN AND DEVELOPMENT
TITLE TDU-GC CABINET LAYOUT
MATERIAL
NO REQ'D 1
TOLERANCES
SCALE
SHEET 10 OF 17
DECIMAL ±
FRACTIONS ±
CONTRACT
DATE 3-15-82
ANGLES ±
DRAFTSMAN JIM GREEN
DETAIL NO. 82-EDD-C-010

APPENDIX C

TDU-GC TRANSDUCER CALIBRATIONS

To obtain accurate measurements of the various thermal decomposition parameters, it is necessary to have precise measurement devices that have been accurately calibrated. Therefore, the individual TDU-GC measurement transducers have been calibrated using measuring equipment processing trace-ability to the National Bureau of Standards. In this appendix, the calibration data are presented for those transducers that were described earlier in Section 6 under the heading "Instrumentation Associated with the TDU-GC".

The four thermocouple actuated pyrometer instruments were calibrated with a Leeds & Northrup Model 8662 Potentiometer Certified by Instrulab, Inc., Dayton, Ohio. Both ranges of the Fluke 8030A's were calibrated with a Wavetek Model 220 Certified by T.I.L. Instruments Inc., Dayton, Ohio.

CALIBRATION OF OMEGA DIGITAL THERMOMETER
MODEL 199, TYPE J
SERIAL NO. 22091

Standard (°C)	Meter Reading (mv)
0	0.00
10	0.53
20	1.05
30	1.58
40	2.11
50	2.65
60	3.16
70	3.69
80	4.25
90	4.79
100	5.26
200	10.80
300	15.33
400	21.87
500	27.40
600	33.17
700	39.17
750	42.28
800	45.35

CALIBRATION FLUKE DIGITAL MULTIMETER
(Model 8030A)

Standard (VDC)	Meter Reading (VDC)
00.0000	00.00
00.0100	00.01
00.0200	00.02
00.0400	00.04
00.0800	00.08
00.1000	00.10
00.2000	00.20
00.4000	00.40
00.8000	00.80
01.0000	01.00
02.0000	02.00
04.0000	04.00
07.9960	08.00
09.9950	10.00
11.9920	12.00
13.9900	14.00
17.9870	18.00
19.9740	19.99

OMEGA K-1 THERMOCOUPLE CHROMEL-ALUMEL

(CAIN-316G-24)

Actual Temperature (°C)	Temperature Deviation* (°C)
400	+1.08
600	+0.85
800	+0.57
950	+0.52

*When deviation is plus, add to actual reading. When negative, subtract from actual reading.

CALIBRATION OF OMEGA DIGITAL TEMPERATURE
INDICATOR MODEL 2160A, TYPE K
SERIAL NO. 2388072

Standard (mv)	Meter Reading (°C)
-5.892	-200
-3.542	-100
0.00	±000
0.38	10
0.80	20
1.21	30
1.61	40
2.02	50
2.44	60
2.81	70
3.28	80
3.68	90
4.09	100
8.14	200
12.22	300
16.38	400
20.61	500
24.90	600
29.12	700
33.26	800
37.32	900
41.25	1000
45.10	1100
48.82	1200

CALIBRATION OF FLUKE DIGITAL MULTIMETER
(Model 8030A)

Standard (mv)	Meter Reading (mv)
000.00	000.0
000.10	000.1
000.20	000.2
000.30	000.3
000.40	000.4
000.50	000.5
000.60	000.6
000.70	000.7
000.80	000.8
000.90	000.9
001.00	001.0
002.00	002.0
003.00	003.0
004.00	004.0
005.00	005.0
006.00	006.0
007.00	007.0
008.00	008.0
009.00	009.0
010.00	010.0
020.00	020.0
030.00	030.0
040.00	040.0
049.97	050.0
059.97	060.0
069.98	070.0
079.98	080.0
089.98	090.0
099.95	100.0
100.90	101.0
101.90	102.0
102.90	103.0
103.90	104.0
104.90	105.0
105.90	106.0
106.90	107.0
107.90	108.0
108.90	109.0
109.90	110.0
119.90	120.0
129.90	130.0
139.90	140.0
149.90	150.0
159.90	160.0
169.90	170.0
179.85	180.0
189.80	190.0
190.80	191.0
191.80	192.0
192.80	193.0
193.80	194.0
194.80	195.0
195.80	196.0
196.80	197.0
197.80	198.0
198.80	199.0

APPENDIX D

COMPONENTS AND PARTS USED IN TDU-GC SYSTEM

DESCRIPTION	PART NO.	SUPPLIER	ADDRESS	TELEPHONE
Instrumentation Console and Panels	AFCB-1952-25	Cabtron Systems, Inc.	200 Aneta Drive Northbrook, IL 60062	(312) 498-6090
Glove box	Custon Design (see Page 30)	Dayton Plastics, Inc.	2554 Needmore Road Dayton, OH 45377	(513) 276-3921
Gas Chromatograph	Vista 44	Varian Instrument Group	2700 Mitchell Drive Walnut Creek, CA 94598	(415) 939-2400
Potentiometric Recorder	Series 5000 (#5211-4)	Houston Instruments	4950 Terminal Avenue Bellaire, TX 77401	(713) 667-7403
Compressed gases	Various gas cylinders	Matheson Gas Products	8135 Uehling Lane Dayton, OH 45424	(513) 236-3021
Furnace and Controller (3-zones)	54357, furnace 59744-A controller	Lindberg Company	304 Hart Street Watertown, WI 53094	(414) 261-7000
Flow Control Valve	VCD-1000, A-60	Porter Instrument Co., Inc.	P.O. Box 326 Township Line Road Hatfield, PA 19440	(215) 723-4835
Sampling syringes	Series C Syringes	Precision Sampling Corp.	P.O. Box 15119 Baton Rouge, LA 70815	(504) 924-1720
Open Tubular Gas Chromatographic Columns	DB-1 and DB-5 capillary columns	J and W Scientific	3871 Security Park Dr. Rancho Cordova, CA 95670	(916) 351-0387
tubing, transfer	nickel and copper tubing 1/16" + 1/8" O.D.	Applied Science	2051 Waukegan Road Deerfield, IL 60015	(312) 948-8600
Filter, Hydro-purge	14503	Applied Science	2051 Waukegan Road Deerfield, IL 60015	(312) 948-8600
Oxygen traps	14563, 14636	Applied Science	2051 Waukegan Road Deerfield, IL 60015	(312) 948-8600
Fused Quartz Stock	tubing and rod of various sizes	Quartz Scientific, Inc.	819 East Street Fairport Harbor, OH 44077	(216) 354-2186
Pressure transducer	PL-295TC-15-350	Statham Instruments, Inc.	2230 Statham Boulevard Oxnard, CA 90303	(805) 486-8302
Flow transducer	5810	Brooks Instrument Division Emerson Electric Company	Hatfield, PA 19440 c/o King Associates 8737 Tiburon Drive Cincinnati, OH 45242	(513) 984-5550
Temperature Programmer (TECO)	TP-2000-TBX-R2-P1-36	Theall Engineering Company	Box 362 Oxford, PA 19363	(215) 932-3488
Pyroprobe	CDS-120	Chemical Data Systems, Inc.	Oxford, PA 19363	(215) 932-3636
Quartz Wool	- -	Quartz Scientific, Inc.	819 East Street Fairport Harbor, OH 44077	(216) 354-2186
Quartz heating tape	5955-J20	Authur H. Thomas Co.	Vine St. at Third P.O. Box 779 Philadelphia, PA 19105	(215) 574-4555
Glass & Quartz insulation tape	1701, 1790	Wale Apparatus Company	400 Front Street P.O. Box D Hellertown, PA 18055	(215) 838-7047
Thermocouples	Chromel-Alumel (sheathed & unsheathed) GG-K-24SB	Omega Engineering, Inc.	One Omega Drive P.O. Box 4047 Stamford, CT 06907	(203) 359-7700
Glass Adhesive Tape	Tape 27	3M Company	Electro Products Div. St. Paul, MN 55101	(513) 253-1774
Liquid Nitrogen Coolant	LN_2 cylinders	Liquid Carbonic Corp	Springfield Oxygen Div Springfield, OH	(513) 274-85[illegible]
Flow Control Valves (heat transfer air)	"H" Series	Nupro Company	4800 East 345th Street Willoughby, OH 44094	(513) 461-[illegible]

DESCRIPTION	PART NO.	SUPPLIER	ADDRESS	TELEPHONE
Ceramic fiber insulation	WRP-XA-AW Felt	Refractory Products Co.	120 S. Lincoln Ave. Carpentersville, IL	
Charcoal traps	226-01	SKC Inc.	RD 1 395 Valley View Road Eighty Four, PA 15330	(216) 431-7971
Digital VOM	8030A	Fluke, Inc.	c/o National Instrument Distributors 7913 S. Suburban Road Dayton, OH 45459	(513) 435-4503
Thermocouple selector switch	MTG-OSW3-18	Omega Engineering, Inc.	One Omega Drive Box 4047 Stamford, CT 06907	(203) 359-7700
Reactor Temperature readout	2160 K	Omega Engineering, Inc.	One Omega Drive Box 4047 Stamford, CT 06907	(203) 359-7700
Temperature (digital readout)	199 KC-X-X	Omega Engineering, Inc.	One Omega Drive Box 4047 Stamford, CT 06907	(203) 359-7700
Temperature Controller (transfer line)	1400 Series	Gulton Industries, Inc.	Gulton Industrial Park East Greenwich, RI 02818	(401) 884-6800
Gas Switching Valve	5511	Carle Instruments, Inc.	1200 Knollwood Circle Anaheim, CA 92801	(714) 761-9000
Barometer	S-4565	Sargent-Welch Scientific Co.	10400 Taconic Terrace Cincinnati, OH 45215	(513) 241-2243
Rubber Gloves (for glove box)	92-049	Fisher Scientific Co.	5481 Creek Road Cincinnati, OH 45242	(513) 793-5100
Cocoanut Charcoal	5-685	Fisher Scientific Co.	5481 Creed Road Cincinnati, OH 45242	(513) 793-5100
Reagents of Solvents	variety of chemicals	J.T. Baker Chemicals	799 Roosevelt Road Glen Ellyn, IL 60137	(312) 469-4224
Pressure regulators	single and double diagram IL and 8 series	Matheson Gas Products	8135 Uehling Lane Dayton, OH 45424	(513) 236-3021
Stainless Steel restrictor stock	0.010" by 100' #316S.S.	Superior Tube Co.	Norristown, PA 19404	(215) 489-7221
Silicone septa	2-0668	Supelco, Inc	Supelco Park Bellefonte, PA 16823	(814) 359-2784
Tube fittings and ferrules	assorted tube fittings (S.S. and brass)	Crawford Fitting Co.	c/o Cincinnati Valve & Fitting 3710 Southern Avenue Cincinnati, OH 45227	(513) 461-5868
Chemical Standards	various pure samples	Ultra Scientific Inc.	Hope, RI 02831	(401) 828-9400